Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Mesogens Based on Cholesterol Derivatives: Synthesis and Characterization

Ashwini Pandey [a] & Bachcha Singh [a]
[a] Department of Chemistry, (Centre of Advanced Study), Faculty of Science, Banaras Hindu University, Varanasi, India
Version of record first published: 30 Jul 2012.

To cite this article: Ashwini Pandey & Bachcha Singh (2012): Mesogens Based on Cholesterol Derivatives: Synthesis and Characterization, Molecular Crystals and Liquid Crystals, 562:1, 166-176

To link to this article: http://dx.doi.org/10.1080/15421406.2012.687323

Mol. Cryst. Liq. Cryst., Vol. 562: pp. 166–176, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.687323

Mesogens Based on Cholesterol Derivatives: Synthesis and Characterization

ASHWINI PANDEY AND BACHCHA SINGH*

Department of Chemistry, (Centre of Advanced Study), Faculty of Science, Banaras Hindu University, Varanasi, India

A new series of liquid crystals involving cholesterol based mesogenic units and Schiff base moiety interlinked through ester linkage were designed and synthesized. The target compounds were obtained by the reaction of 4′-(3-cholesteryl oxy carbonyl)benzaldehyde with different substituted aromatic and heterocyclic amines. The molecular structures of the compounds were confirmed by Fourier transform infrared (FT-IR), ^{1}H, and ^{13}C nuclear magnetic resonance spectra. The mode of linkage has been made via −COO− and −C=N− bonds. The linkages and different substituted aromatic and heterocyclic groups were undertaken to study their influence on the isotropization temperature (Ti) and on mesomorphic property. The thermal phase behavior of the synthesized compounds was investigated by polarizing optical microscopy coupled with hot stage and differential scanning calorimetry (DSC). Enantiotropic cholesteric phase were shown by 4′-[3-Cholesteryloxycarbonyl]benzylidene- 1, 2, 4-triazine-3-yl and monotropic nematic mesophase were shown by 4′-[3-Cholesteryl oxycarbonyl]benzylidene-(4- methyl)aniline whereas 4′-[3-Cholesteryloxycarbonyl] benzylidene-(4-butoxycarbonyl)aniline defined oily streak phase in heating cycle. The remaining members of the series exhibited monotropic droplet texture in cooling cycle with exclusive suppression of cholesteric phase.

Keywords Cholesterol based Schiff′s base; differential scanning calorimetry; enantiotropic mesophase; mesogenic units; monotropic mesophase; polarizing optical microscopy; synthesis

1. Introduction

Cholesterol-based liquid crystals have attracted attention of researchers, not only due to the fact that cholesterol is wide-spread in nature and commercially available, but also because of the helical supermolecular structure of cholesterol-based liquid crystals impart some unique optical properties, such as selective reflection of circularly polarized light, high optical rotatory power, circular dichroism, and electro-optic effect [1]. Additionally, these properties are dependent on conditions such as temperature, pressure, and electric field and thus they could be potential candidates for applications in optical storage, color display techniques and full color rewritable recording devices [2–4].

The work has been presented in oral lecture session of "National Symposium on Advanced Functional Materials (NSAFM 2012)" held in the Department of Chemistry of Banaras Hindu University on 11th and 12th February 2012.

*Address correspondence to Bachcha Singh, Department of Chemistry, Faculty of Science, BHU, Varanasi-221005, India. Tel: +915426702475; Fax: 05422368127. E-mail: bsinghbhu@rediffmail.com

The C3-hydroxyl group of cholesterol allows the synthesis of various cholesteryl esters or ethers. Such compounds are widely utilized in toiletries and cosmetics, pharmaceuticals, and chemical industry [5]. Both the rigid steroid skeleton and its hydrophobic nature create a tendency of such molecules to aggregate into large three-dimentional structures in which the position and orientation of the molecule is organized [6,7].

Cholesterol itself modulates the structural and dynamic properties of phospholipid double-layer membranes [7].

Due to its rigid structure with eight chiral centers and the ease with which the structure can be derivatized, cholesterol has been incorporated extensively in chiral liquid crystalline materials. The ability of cholesterol in inducing a liquid crystalline property in its various derivatives motivated many researchers to synthesize thousands of monomers, oligomers, and polymers, based on cholesterol [8].

Imrie et al. have published some critical reviews [9–11], which systematically describe the relationships between molecular structure and mesomorphic behavior. The dimers [12–28] and trimers [29–32] consisting of cholesteryl ester unit as chiral segment joined to different mesogenic moieties such as benzoate ester, Schiff′s base, azobenzene , biphenyl or tolane, etc., through flexible spacers have been synthesized and exclusively studied.

Itahara et al. [33] reported the liquid crystalline materials by connecting adenine or thymine to cholesteryl benzoate or related steroid groups throughpolymethylenespacer.

Yellamaggad et al. [34] also reported the liquid crystalline properties of dimesogenic compounds in which one of the mesogenic units was the cholesterol moiety.

Here, we report Synthesis and characterization of new mesogenic compounds containing aromatic and heterocyclic moieties connected to a cholesteryl ester moiety through Schiff base linkage.

2. Experimental Details

2.1 Materials

Thionyl chloride and pyridine (Qualigens) were used as received. 4-Formylbenzoic acid, cholesterol p-toludine, p-anisidine, methyl p-aminobenzoate, ethyl p-aminobenzoate, butyl p-aminobenzoate, and 3-amino-1,2,4-triazine were procured from Sigma-Aldrich Chemicals, USA and were used as received. All other solvents and reagents were AR grade and used without further purification.

2.2 Techniques

Elemental analyses were performed on a CE-440 Exeter Analytical CHN analyzer. IR spectra were performed on an FT-IR Varian 3100 Excalibur series spectrophotometer in KBr pellet in the 4000–100 cm^{-1} region. ^{1}H and ^{13}C nuclear magnetic resonance spectra were obtained on a JEOL FT-NMR AL 300 MHz spectrometer using tetramethylsilane as the internal standard. Differential scanning calorimetry (DSC) thermograms were recorded with a Mettler Toledo TC15 TA differential scanning calorimeter at the rate of 10.0 K min^{-1} under a nitrogen atmosphere using spec pure grade indium as standard by taking samples in close lid aluminum pans. The transition temperatures from DSC have been determined with an accuracy of ± 0.1 K. The mesophase type of the compounds were identified by visual comparison with known phase standards using an HT 30.01 NTT 268 Lomo polarizing optical microscope (POM) fitted with a hot stage with temperature controlling accuracy of 0.1 K.

2.3. Synthesis of Compounds

2.3.1 Synthesis of 4′-(3-Cholesteryloxycarbonyl)benzaldehyde (3). 4-Formylbenzoic acid (1.5 g, 10 mmol) (**1**) was dissolved in dry THF (50 ml), and thionyl chloride (2.4 g, 20 mmol) was added and refluxed for 7 h. The solvent and excess thionyl chloride was removed under reduced pressure to give 4-formylbenzoyl chloride (**2**) as yellow oil. The acid chloride (**2**) was treated with cholesterol (3.86 g, 10 mmol) in dry THF (50 ml) containing 2–3 drops of pyridine. The reaction mixture was refluxed for 8 h resulting in a deep yellow color solution. The solvent was removed under reduced pressure to give a cream color product, which was washed four times with water (50 ml) dried and recrystallized from chloroform to afford 4′-(3-cholesteryloxycarbonyl)benzaldehyde (**3**) as crystals. Yield: 75%. FT-IR (KBr, cm^{-1}): 2936, 2899, 2866 (aliphatic C−H stretching), 1737 (C=O ester), 1705 (C=O aldehyde), 1637, 1575(Ph), 1463 (aromatic C=C), 1378, 1276. ^{1}H NMR ($CDCl_3$) δ_H (ppm): 10.10 (s, 1H, CHO), 8.25–8.18 (d, 2H, ArH), 7.95–7.92 (d, 2H, ArH), 5.35 (m, 1H, −C=CH−), 3.54 (t, 1H, OC<u>H</u>−CH_2), 2.27 (q, 2H, OCH−C<u>H</u>$_2$), 2.03–0.67 (m, 41H, −CH, −CH_2 and CH_3). ^{13}C NMR ($CDCl_3$) δ_c (ppm): 191.6 (<u>C</u>HO), 167.0 (<u>C</u>OO), 140.7, 130.0, 129.4, 129.3, 122.9, 121.4, 77.4, 77.0, 76.5 ($CDCl_3$) 75.2, 71.5, 56.6, 56.5, 56.0, 50.0, 42.2, 39.6, 39.4, 37.1, 36.5, 36.0, 35.6, 31.7, 28.1, 27.9, 24.1, 23.7, 22.7, 22.4, 20.9, 19.3, 18.6, 11.7. Elemental analyses: calculated for $C_{35}H_{48}O_3$ (%), C, 81.03; H, 9.71; Found, C, 80.92; H, 9.38.

2.3.2. Synthesis of 4′-(3-cholesteryloxycarbonyl)benzylidene- (4-methyl)aniline (4a). To a solution of 4′-(3-cholesteryloxycarbonyl) benzaldehyde (**3**) (2.59 g, 5 mmol) in chloroform (30 ml) was added (0.53 g, 5 mmol) of 4-methylaniline (0.53g, 5 mmol) and 2–3 drops of glacial acetic acid. The reaction mixture was refluxed for 6 h and then cooled to give a deep yellow color product. The compound was washed 2–3 times with distilled water (25 ml) then with ethanol (50 ml) two times and dried. Yield: 75%. FT-IR (KBr, cm^{-1}): 2935, 2853 (aliphatic C−H stretching), 1711, 1643 (C=N), 1462, 1375, 1274, 1191, 1112, 1051, 954, 810. ^{1}H NMR ($CDCl_3$) δ_H (ppm): 8.52 (s, 1H, CH=N), 8.13–7.18 (m, 8H, ArH), 5.35 (m, 1H, −C=CH−), 3.56 (t, 1H, −OC<u>H</u>−CH_2), 2.38 (q, 2H, −OCH−C<u>H</u>$_2$), 2.35 (t, 3H, −C<u>H</u>$_3$$C_6H_4$N=CH−) 2.22–0.67 (m, 41H, −CH, −CH_2 and CH_3). ^{13}C NMR ($CDCl_3$) δ_c (ppm): 167.0, 163.7, 140.7, 129.8, 128.4, 122.8, 121.7, 120.8, 77.4, 77.0, 76.5 ($CDCl_3$) 74.9, 71.7, 56.7, 56.1, 50.0, 42.2, 39.7, 39.4, 37.2, 36.4, 36.1, 35.7, 31.8, 31.6, , 29.6, 28.2, 27.9, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.6, 11.8. Elemental analyses: calculated for $C_{42}H_{57}NO_2$ (%) C, 82.98; H, 2.30; N, 2.30; Found, C, 82.63; H, 8.98; N, 2.16.

The procedure for the preparation of 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-methoxy)aniline (**4b**), 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-methoxycarbonyl)aniline (**4c**), 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-ethoxycarbonyl)aniline (**4d**), 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-butoxycarbonyl)aniline (**4e**), and 4′-(3-cholesteryloxy carbonyl)benzylidene-3-amino-1, 2, 4-triazine (**4f**) are similar to that described above,

2.3.3. 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-methoxy)aniline (4b). Yellow powder (Yield: 61%). FT-IR (KBr, cm^{-1}) 2852, 2831 (aliphatic C−H stretching), 1731, 1641 (C=N), 1450, 1371, 1272, 1185, 1121, 1052, 972, 815. ^{1}H NMR ($CDCl_3$) δ_H (ppm): 8.53 (s, 1H, −CH=N−), 8.13–6.93 (m, 8H, ArH), 5.35 (m, 1H, −C=CH−), 3.56 (t, 1H, −OC<u>H</u>−CH_2), 2.50 (q, 2H, −OCH−C<u>H</u>$_2$), 2.22–0.67 (m, 41H, −CH, −CH_2 and CH_3). ^{13}C NMR ($CDCl_3$) δ_c (ppm): 163.9, 160.1, 158.6, 140.7, 129.8, 122.3, 121.6, 114.4, 77.4, 77.0, 76.5 ($CDCl_3$), 71.7, 56.7, 56.6, 56.0, 55.4, 50.0, 42.2, 39.7, 39.4, 37.2, 36.4, 36.1, 35.7, 31.9, 31.8, 31.7, 31.6, 29.6, 28.2, 27.9, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.6, 11.8.

Elemental analyses: calculated for $C_{42}H_{57}NO_3$ (%) C, 80.85; H, 9.20; Found, C, 80.62; H, 8.91; N, 1.84.

2.3.4 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-methoxycarbonyl)aniline (4c). Yellow powder (Yield: 60%). FT-IR (KBr, cm^{-1}) 2934, 2824 (aliphatic C−H stretching), 1715, 1642 (C=N), 1458, 1372, 1219, 1171, 1109, 1051, 960, 844. ^{1}H NMR ($CDCl_3$) δ_H (ppm): 8.49 (s, 1H, −CH=N−), 8.15-6.91 (m, 8H, ArH), 5.43 (m, 1H, −C=CH−), 4.33 (t, 1H, −OCH−CH_2), 2.50 (q, 2H, −OCH−CH_2), 2.20–0.67 (m, 41H, −CH, −CH_2, and CH_3). ^{13}C NMR ($CDCl_3$) δ_c (ppm): 166.0, 160.6, 139.5, 130.9, 129.9, 128.8, 122.9, 120.6, 77.4, 77.0, 76.5 ($CDCl_3$), 75.0, 56.6, 56.1, 42.3, 39.5, 36.6, 36.1, 35.7, 31.8, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8. Elemental analyses: calculated for $C_{43}H_{57}NO_4$ (%) C, 79.22; H, 8.81; N, 2.14; Found C, 78.90; H, 8.43; N, 2.13.

2.3.5 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-ethoxycarbonyl)aniline (4d). Yellow powder (Yield: 65%). FT-IR (KBr, cm^{-1}) 2938, 2831 (aliphatic C−H stretching), 1710, 1643 (C=N), 1604 (Ph), 1517, 1464, 1372, 1219, 1171, 1109, 1051, 955, 844, 770. ^{1}H NMR ($CDCl_3$) δ_H (ppm): 8.48 (s, 1H, −CH=N−), 8.15–6.62 (m, 8H, ArH), 5.35 (m, 1H, −C=CH−), 4.40 (t, 1H, −OCH−CH_2), 2.50 (q, 2H, −OCH−CH_2), 2.22–0.67 (m, 41H, −CH, −CH_2, and CH_3). ^{13}C NMR ($CDCl_3$) δ_c (ppm): 167.3, 165.4, 160.5, 155.6, 139.5, 139.3, 133.5, 130.8, 129.9, 128.7, 128.2, 122.9, 120.6, 77.4, 77.0, 76.5 ($CDCl_3$), 75.0, 64.8, 56.5, 56.2, 50.0, 42.3, 39.7, 39.4, 38.1, 37.0, 36.5, 35.8, 30.8, 28.0, 27.8, 24.2, 23.8, 22.7, 22.5, 21.0, 19.3, 19.2, 18.7, 13.7, 11.8. Elemental analyses: calculated for $C_{44}H_{59}NO_4$ (%) C, 79.35; H, 8.92; N, 2.10; Found, C, 78.95; H, 8.65; N, 2.15.

2.3.6 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-butoxycarbonyl)aniline (4e). Yellow powder (Yield: 68%). FT-IR (KBr, cm^{-1}) 2935, 2903, 2869 (aliphatic C−H stretching), 1738, 1710, 1630 (C=N), 1597 (Ph), 1464, 1379, 1274, 1193, 1166, 1106, 1057, 1014, 958, 889, 859, 774. ^{1}H NMR ($CDCl_3$) δ_H (ppm): 8.48 (s, 1H, −CH=N−), 8.15–7.95 (m, 8H, ArH), 5.43 (m, 1H, −C=CH−), 4.33 (t, 1H, −OCH−CH_2), 2.50 (q, 2H, −OCH−CH_2), 2.20–0.67 (m, 41H, −CH, −CH_2, and CH_3). ^{13}C NMR ($CDCl_3$) δ_c (ppm): 166.3, 165.3, 160.5, 155.6, 139.5, 139.3, 133.5, 130.8, 129.9, 128.7, 128.2, 122.9, 120.6, 77.4, 77.0, 76.5 ($CDCl_3$), 64.8, 56.6, 56.1, 50.0, 42.3, 39.7, 39.5, 38.1, 37.0, 36.1, 35.7, 31.8, 30.8, 28.2, 28.0, 27.8, 24.2, 23.8, 22.8, 22.5, 21.0, 19.2, 18.7, 13.7, 11.8. Elemental analyses: calculated for $C_{46}H_{63}NO_4$ (%) C, 79.61; H, 9.14; N, 2.01; Found, C, 79.18; H, 9.11; N, 1.81.

2.3.7. 4′-(3-Cholesteryloxycarbonyl)benzylidene- 3-amino-1,2,4-triazine (4f). Yellow powder (Yield: 64%.) FT-IR (KBr, cm^{-1}) 2950, 2903, 2869 (aliphatic C−H stretching), 1738, 1710, 1630 (C=N), 1597 (Ph), 1464, 1379, 1276, 1201, 1112, 1015, 980, 821, 793.^{1}H NMR ($CDCl_3$) δ_H (ppm): 10.09 (s, 1H, −CH=N−), 8.20–7.92 (m, 6H, ArH), 5.42 (m, 1H, −C=CH−), 4.30 (t, 1H, −OCH−CH_2), 2.46 (q, 2H, −OCH−CH_2), 2.00–0.69 (m, 41H, −CH, −CH_2 and CH_3). ^{13}C NMR ($CDCl_3$) δ_c (ppm): 191.7, 166.0, 160.1, 149.0, 145.6, 130.1, 129.4, 77.4, 77.0, 76.5 ($CDCl_3$), 75.3, 56.6, 56.1, 39.5, 36.4, 31.9, 28.2, 28.0, 27.8, 24.2, 23.8, 22.8, 22.5, 18.7, 11.8. Elemental analyses: calculated for $C_{38}H_{52}N_4O_2$ (%), C, 76.47; H, 8.78; N, 9.38; Found, C, 76.21; H, 8.27; N, 9.14.

3. Results and Discussion

The synthetic route for the preparation of cholesterol based mesogens are outlined in Scheme 1. The elemental analyses, FT-IR and NMR spectra are fully consistent with the structure. The compound 4′-(3-cholesteryloxy carbonyl)benzaldehyde (**3**) exhibits major bands at 2936, 2899, 2866 ν(C−H aliphatic), 1737 ν(C=O ester), 1705ν(C=O aldehyde), 1637 ν(Ph), 1575 cm^{-1} ν(C=C aromatic) stretch. The compound (**3**) after condensation with p-toludine displays major IR bands at 2935, 2853 ν(C−H aliphatic), 1711 ν(C=O ester), 1643 ν(C=N). The disappearance of band at 1705 cm^{-1} due to ν(CHO) and appearance of a new band at 1643 cm^{-1} due to ν(C=N) indicates condensation of aldehyde with amine forming Schiff base and confirming the structure of the compound 4′-(3cholesteryloxycarbonyl)benzylidene- (4-methyl)aniline (**4a**).

The proton NMR of 4′-(3-cholesteryloxycarbonyl)benzaldehyde (**3**) depicts signals at δ10.10 (s), 8.25–8.18 (d), 7.95–7.92 (d), 5.35 (m) , 2.27 (q), 2.03-0.67 (m) ppm that are attributed to −C<u>H</u>O, ring, −C=C<u>H</u>− , −OCH−C<u>H</u>$_2$, methyne, methylene, and methyl protons of cholesterol moiety, respectively. The proton NMR of 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-methyl)aniline (**4a**) displays signals at 8.52 (s, 1H, −CH=N), 8.13–7.18 (m, 8H, ArH), 5.35 (m, 1H, −C=CH−), 3.56 (t, −OC<u>H</u>−CH_2), 2.38 (q, 2H, −OCH−C<u>H</u>$_2$), 2.22–0.67 (m, 41H, -CH, -CH_2 and CH_3) ppm respectively. The characteristic signal due to azomethine group is observed at 8.52 ppm that confirms the formation of 4′-(3-cholesteryloxycarbonyl)benzylidene–(4-methyl)aniline (**4a**). The ^{13}C NMR spectrum of the compound 4′-(3-cholesteryloxy carbonyl)benzaldehyde (**3**) exhibits signals at δ 191.6 for −<u>C</u>HO bonded to an aromatic ring , 167.0 for <u>C</u>OO ester, 140.7, 130.0, and 129.4 for aromatic ring, signals 77.4, 77.0, 76.5 for $CDCl_3$. The signals for the carbons of the cholesterol moiety are listed in the synthetic part. The compound 4′-(3-cholesteryloxycarbonyl)benzylidene-(4-methyl)aniline (**4a**) dispays major ^{13}C NMR signals at δ 167.0 (–<u>C</u>OO ester), 163.7 (azomethine carbon −<u>C</u>H=N) and 140.7, 130.0, 129.8 (carbons of aromatic ring). Thus, the appearance of a new ^{13}C NMR signal, characteristic of azomethine carbon (<u>C</u>H=N) (**4a**) is observed δ 163.7, which confirms the formation of Schiff base (**4a**).

All other members of the series (**4b–4f**) exhibit similar IR, NMR (^{1}H and ^{13}C) bands are listed in the synthesis.

4. Optical Properties

The phase transitions of the new mesogenic compounds **4a–4e** were measured using DSC at the rate of 10.0 K min^{-1}. The transition temperatures and associated enthalpies obtained are shown in Table 1. Textural analyses were performed with the help of a POM. The compound **4a** exhibited polymorphic changes in the heating cycle with the appearance of several endothermic peaks while in cooling cycle it displayed nematic phase with the appearance of exothermic peak centered at 226.7°C (ΔH = 0.56 KJ mol^{-1})(ΔS = 1.12 JK^{-1} mol^{-1}) (ΔS = 1.48 JK^{-1} mol^{-1}). Under optical microscope a monotropic nematic phase observed for this compound was judged by the appearance of numerous globular radial bubbles (nematic droplets) (Fig. 1). Then, this sharply transformed to a crystal phase centered at 224.4°C (ΔH = 0.74 kJ mol^{-1}, ΔS = 1.48 JK^{-1} mol^{-1}) followed by successive crystal phases in cooling cycle. Similar patterns were observed for the compounds **4b**, **4c**, and **4d** also.

The compound **4b** exhibited successive endothermic peaks in the heating cycle with more polymorphic changes and a similar isotropization temperature (T_i), centered at

Table 1. Transition temperatures of cholesterol based mesogens

Compounds	Transition temperatures (°C)
4a	Cr_1 65.4 (0.22)*(0.65)** Cr_2 68.6 (0.97) (2.83) Cr_3 107.2(0.86) (2.26) Cr_4 138.6 (37.82) (91.81) $Cr_5$147.3 (1.09) (2.59) Cr_6 172.3 (0.16)(0.35) Cr_7 187.16 (1.02) (2.21) Cr_8 227.19 (1.30) (2.59) I 226.75 (0.59)(1.12) N 224.4 (0.74) (1.48) Cr_8 184.2 (0.60) (1.13) Cr_7 178.7 (0.60) (1.32) Cr_6 144.0 (1.23) (2.94) Cr_5 144.0 (28.76) (68.95) $Cr_4$62.5 (1.25) (3.75) Cr.
4b	Cr_1 68.6 (1.77)*(5.18)** Cr_2 107.6 (1.59) (4.17) Cr_3 129.9 (1.27) (3.15) Cr_4 142.7 (32.11) (77.23) Cr_5 147.3 (0.88) (2.09) Cr_6 187.3(1.10) (2.38) Cr_7 227.19 (1.26) (2.51) I 224.5(1.11) (2.23) N 214.5 (0.45) (0.92) Cr_7 184.0 (0.77) (1.68) Cr_6 144.25 (1.24) (2.97) Cr_5 104.8 (36.97) (97.83) Cr_4 74.8 (0.54) (1.55) Cr_3 61.92 (0.84) (2.50) Cr.
4c	Cr_1 68.8 (2.92)*(8.54)** Cr_2 107.3 (0.89) (2.34) $Cr_3$146.8 (1.75) (4.16) Cr_4 179.3(14.99) (33.14) $Cr_5$186.6 (0.88) (0.87) (1.19) Cr_6 227.4 (1.88) (0.37) I 224.5 (1.57) (3.15) N 184.0 (1.84) (4.02) Cr_6 227.4 (1.88) (0.37) I 224.5 (1.57) (3.15) N 184.0 (1.84) (4.02) Cr_6 144.0 (1.92) (4.61) Cr_5 127.62 (1.56) (3.96) Cr_4 104.5. (2.53) (6.70) Cr_3 62.0 (1.23) (3.67) Cr.
4d	Cr_1 65.6 (0.05)*(0.15)** Cr_2 68.6 (0.69) (2.01) Cr_3 89.7 (0.07) (0.19) Cr_4 107.4 (0.92) (2.41) Cr_5 147.3 (0.45) (1.07) Cr_6 186.6 (0.35) (0.77) Cr_7 227.1 (0.42) (0.83) Cr_8 268.1 (0.69) (1.27) Cr_9 309.4 (0.76) (1.30) I 307.1 (0.51) (0.87) N 265.6 (0.40) (0.74) Cr_9 224.5 (0.38) (0.76) Cr_8 104.5 (1.02) (2.71) Cr_7 59.42 (0.12) (0.38) Cr.
4e	Cr_1 68.6 (2.71)*(7.93)** Cr_2 107.4.6 (2.44) (6.41) Cr_3 124.8 (18.60) (46.75) Cr_4 147.0 (2.81) (6.69) Cr_5 187.0 (2.66) (5.78) N* 227.4 (2.07) (4.13) I 224.3 (2.29) (4.60) Cr_5 184.05 (1.60) (3.50) Cr
4f	Cr_1 49.6 (5.78)*(17.91)** Cr_2 68.7 (0.82) (2.41) Cr_3 119.2 (2.58) (6.57) Cr_4 147.1 (0.55) (1.32) Cr_5 186.6 (0.29) (0.63) SmA 224.1 (0.06) (0.13) N* 227.1 (0.59) (1.17) I 184.2 (0.58) (1.26) N* 144.2 (0.75) (1.79) Cr_5 104.5 (0.91) (2.42) Cr_4 73.0 (0.24) (0.69) Cr_3 62.44 (0.64) (1.90) Cr

*The value in parentheses denotes enthalpy in kJ mol^{-1}.

**The value in parentheses denotes entropy in JK^{-1} $mol^{-1.}$

where Cr signifies crystal phase , Sm A signifies smectic A phase , N signifies nematic phase, N* signifies chiral nematic phase (cholesteric phase), and I signifies the isotropic liquid phase.

227.1°C in the heating cycle compared to the isotropization temperature (T_i) of **4a**. The compounds **4c** and **4d** exhibited a successive increase in isotropization temperature (Ti), which was noticed at 227.4°C for **4c** and 309.4°C for **4d**. A similarity in polymorphism was noticed for the appearance of exothermic peaks in cooling cycle for compounds **4b** and **4c** respectively. For the compound **4d**, an incremental enhancement in the polymorphic behavior was noticed with the appearance of successive endothermic and exothermic peaks in both the heating and cooling cycles compared to that of **4b** and **4c**.

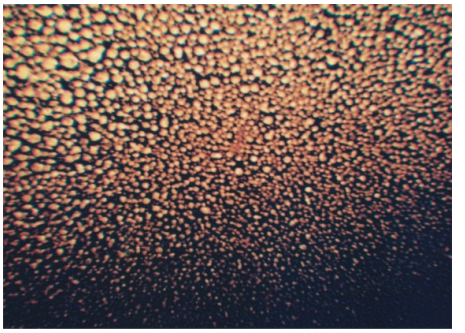


Figure 1. Microphotograph of the nematic droplets of the compound 4′-[3-Cholesteryloxy carbonyl]benzylidene- (4-methyl)aniline (**4a**) at 226.7°C in cooling cycle.

Thus, the compounds **4b**, **4c**, and **4d** exhibited a similar monotropic nematic droplets in cooling cycle centered at 224.5°C ($\Delta H = 1.11$ kJ mol^{-1} $\Delta S = 2.23$ JK^{-1} mol^{-1}), 224.5°C ($\Delta H = 1.57$ kJ mol$^{-1}\Delta S = 3.15$ JK^{-1} mol^{-1}) and 307.1°C ($\Delta H = 0.51$ kJ mol^{-1} $\Delta S = 0.87$ JK^{-1} mol^{-1}), respectively. The monotropic nematic phase transition temperature decreases from **4a** to **4f** in the cooling cycle except **4e** for which it occurs in heating cycle. The compound **4d** shows the phase transition at higher temperature due to increase in chain length. The isotropization temperature is almost same for the compounds except for the compound **4d**, which changes to isotropic state at 309.4°C due to chain length. The monotropic and enantiotropic cholesteric (N*) phases were observed for the compounds **4e** and **4f** as **4e** possesses an increased carbon chain and **4f** possesses a hetrocyclic aromatic moiety. The remaining compounds **4a–4d** showed the cholesteric phase though they do contain a cholesterol moiety. This shows that p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$MeOOCC_6H_4$, and p-$EtOOCC_6H_4$ groups suppress the formation of the N* phase. This is in agreement with the observations reported by Kim and Park [35, 36] where the perfluoroalkoxy group suppressed the formation of the N* phase due to variation in length in the cholesterol containing compounds. The suppression of cholesteric phase has also been reported by other workers [37–39].

The compound **4e** exhibited at characteristic cholestric oily-streak texture with stripes of fine *battons* arranged in layers (beads on string texture) (Fig. 2) at 187.0°C under the

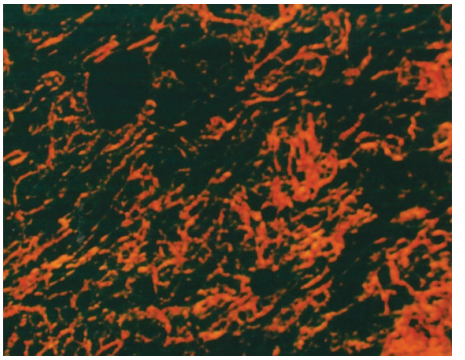


Figure 2. Microphotograph of the compound 4′-[3-Cholesteryloxycarbonyl]benzylidene- (4-butoxycarbonyl)aniline (**4e**) showing oily-streak texture at 187.0°C in heating cycle.

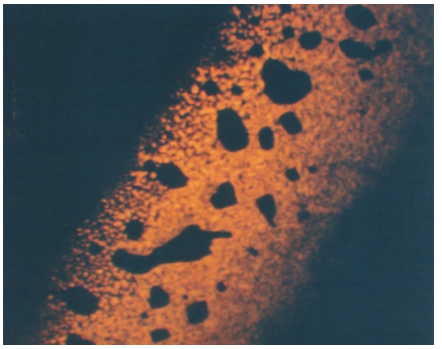


Figure 3. Microphotograph of the compound 4′-[3-Cholesteryloxycarbonyl]benzylidene-1, 2, 4-triazine-3-yl (**4f**) showing smectic A phase at 186.6°C in heating cycle.

POM in heating cycle. A green color in the cholesteric state is also observed. It is well known that the pitch of chiral nematics is dependent on temperature, and that the selective reflection of light occurs when its wavelength is equal to the pitch of the helical structure in the chiral nematic phase. We did not observe colors other than green on increasing the temperature, probably due to the temperature ranges of the chiral nematic phase being narrow. The exothermic peak at 224.3°C for this compound defines transition from isotropic to crystal phase followed by the next crystal phase Thus, the compound **4e** displayed an oily-streak texture of the N* phase only in heating cycle. This is to be noted here that only the virgin sample of compound **4e** exhibited the appearance of green color with the appearance of oily-streak texture in heating cycle. For the successive cycle run of the same compound in heating and cooling cycle no such phenomenon was observed.

The compound **4f** exhibited endothermic peaks at 49.6, 186.6, and 224.1°C owing to crystal to crystal, crystal to SmA and SmA to cholesteric (N*) phase (Fig. 3) transitions respectively . Under optical microscope, a focal-conic texture is seen with dark homeotropic domains, which coalesce to form fan-like texture of cholesteric phase (Fig. 4) in accordance with the reported texture for the cholesteric phase. The transition temperature corresponding to 227.1°C in heating cycle accounts for chiral nematic to isotopic phase transition. The compound **4f** exhibits exothermic peak at 184.2°C because of isotropic to chiral nematic phase (cholesteric phase) (Fig. 5) and the peaks at 144.2,144.3, 104.5, 73.0, and 62.4°C

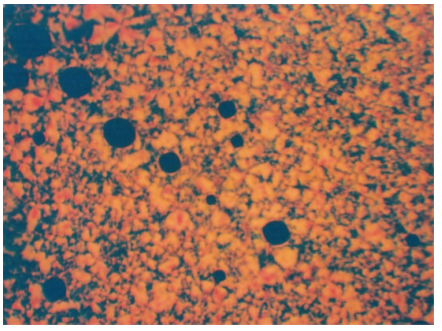


Figure 4. Microphotograph of the compound 4′-[3-Cholesteryloxycarbonyl]benzylidene-1, 2, 4-triazine-3-yl (**4f**) showing cholesteric phase at 224.1°C in heating cycle.

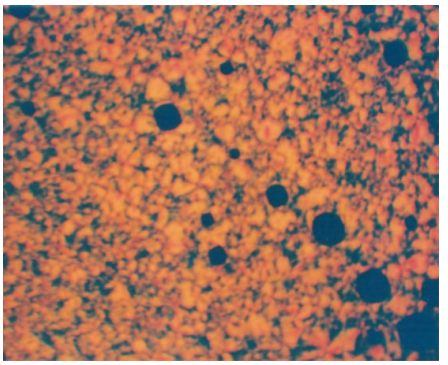
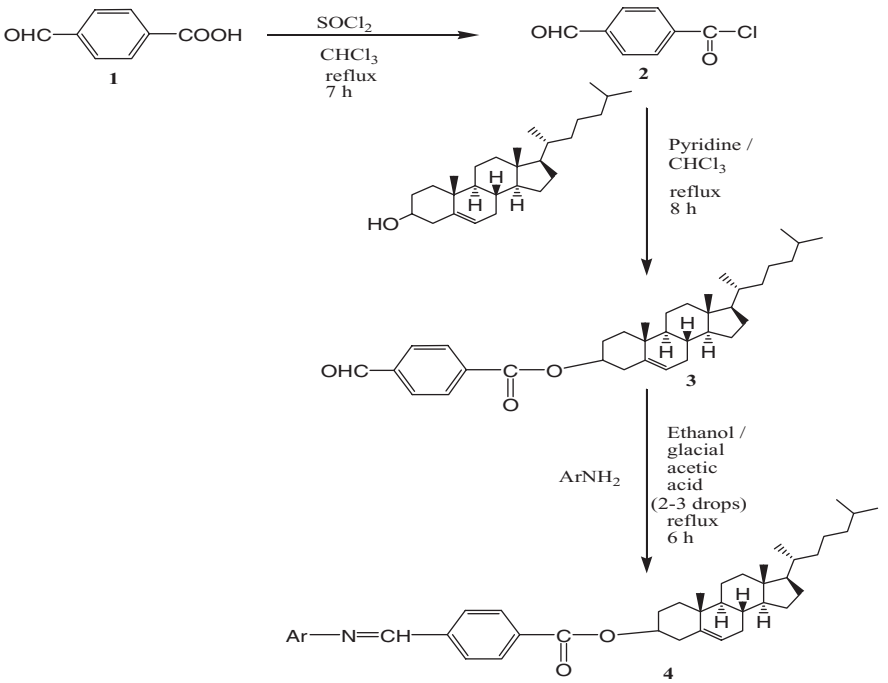


Figure 5. Microphotograph of the compound 4′-[3-Cholesteryloxycarbonyl]benzylidene-1, 2, 4-triazine-3-yl (**4f**) showing cholesteric phase at 184.2°C in cooling cycle.

define successive transition to the crystal phases. The compound **4f** displays smectic A phase only in the heating cycle. This may be due to heterocyclic aromatic group linked to cholesterol moiety. The position of the nitrogen may play important role in layer formation. The lone pair of electrons on the nitrogen atoms act to broaden the molecule and also introduce attractive forces, which leads to smectic phase formation [40].



where Ar = p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$MeOOCC_6H_4$, p-$EtOOCC_6H_4$, p-$BuOOCC_6H_4$, 1,2,4-triazin-3-yl.

Scheme 1. Schematic route for the synthesis of cholesterol based mesogens.

Many cholesterol based compounds in the chiral nematic phase can reflect iridescent colors under the visible light, because the pitch of the helical structure and the wavelength of visible light are of the same order of magnitude, around hundreds of nanometers. However, the compounds **4a**, **4b**, **4c**, **4d**, and **4f** do not reflect brilliant colors owing to the fact that the pitch of the compound is far greater than the wavelength of visible light.

5. Conclusions

A series of novel compounds containing cholesterol and Schiff base groups interlinked through ester bonds were synthesized. The linking group increase the flexibility and mobility of particular part of liquid crystal molecule and produce a higher nematic stability. The linkages and different ring substituted aromatic and heterocyclic groups were undertaken to understand their influence on isotropization temperature and mesomorphic properties. Some of these compounds displayed cholesteric phase with high phase transition temperature over a wide range during heating along with exhibition of green liquid crystalline state because the cholesteric pith length was equal to the wavelength of visible light whereas the remaining members of the homologous series exhibited monotropic nematic droplet in cooling cycle with exclusive suppression of the cholesteric phase in both the cycles though they contain a cholesterol moiety. The isotropization temperature, melting point and the mesomorphic properties are dependent on substituted aromatic and heterocyclic cores.

Acknowledgment

The authors thank the Head of the Department of Chemistry, Banaras Hindu University (BHU), Varanasi for providing laboratory facilities. One of the authors (Ashwini Pandey) thanks the council of scientific and industrial research (CSIR-New Delhi) for financial support as a senior research fellow at BHU, Varanasi. Thanks are also due to the staff of analytical division for C, H, and N analyses and for recording of ^{1}H, ^{13}C NMR and IR spectra.

References

[1] (a) Bobrovsky, A. Y., Boiko, N. I., & Shilaev, V. P. (1998). *Polym. Sci. 40*, 232; (b) Peter, P. M. (1998). *Nature*, *391*, 745 (c) Kurihara, S., Nomiyama, S., & Nonaka, T. (2001). *Chem. Mater.*, *13*, 1992.
[2] Wang, L. Y., & Liao, S. S. (1985). *Liquid Crystal Chemistry*, Science Publication: Beijing, p. 24.
[3] Tamaoki, N. (2001). *Adv. Mater.*, *13*, 1135.
[4] Mallia, V. A., & Tamaoki, N. (2004). *Chem. Soc. Rev.*, *33*, 76.
[5] Urata, K., & Takaishi, N. (1997). Cholesteryl ester compounds containing alkyl branched acyl groups-their preparations, properties and applications. *Fett/Lipid.*, *99*, 327.
[6] Thiemann, T., & Vill, V. (1997). *J. Phys. Chem. Ref. Data*, *26*, 291.
[7] Inoue, K., & Shinkai, S. (1998). *Hyomen*, *36*, 421.
[8] (a) Davis, A. P. (1993). *Chem. Soc. Rev.*, *22*, 243 (b) (2007) *Chem. Soc. Rev.*, *36*, 2096; (c) Yelamaggad, C. V., Hiremath, U. S., Shankar Rao, D. S., & Prasad, S. K. (2000). *Chem, Commun.*, 57.
[9] Imrie, C. T., & Henderson, P. A. (2007). *Chem. Soc. Rev.*, *36*, 2096.
[10] Imrie, C. T., Henderson, P. A., & Yeap, G. Y. (2009). *Liq. Cryst.*, *36*, 755.
[11] Imrie, C. T. (1999). *Struct. Bonding*, *95*, 150.
[12] Yelamaggad, C. V., & Shankar, G. (2007). *Liq. Cryst.*, *34*, 799.

[13] Yelamaggad, C. V., Shankar, A., Rao, D. S. S., & Prasad, Krishna S. (1999). *Liq.Cryst.*, *26*, 1547.
[14] Sharma, R. K., Gupta, V. K., Mathews, M., & Yelamaggad, C. V. (2008). *Liq. Cryst.*, *35*, 1161.
[15] Sharma, R. K., Gupta, V. K., Mathews, M., & Yellamaggad, C. V. (2009). *Liq. Cryst.*, *36*, 225.
[16] Gupta, V. K., Sharma, R. K., Mathews, M., & Yelammagad, C. V. (2009). *Liq. Cryst.*, *36*, 339.
[17] Pandey, A. S., Dhar, R., Pandey, M. B., Achalkumar, A. S., & Yelamaggad, C. V. (2009). *Liq. Cryst.*, *36*, 13.
[18] Hardouin, F., Achard, M. F., Jin, J.-I., & Shin, J.-W. (1994). *J. Phys. II Fr.*, *4*, 627.
[19] Hardouin, F., Achard, M. F., Laguerre, M., Jin, J.-I., & Ko, D.-H. (1999). *Liq. Cryst.*, *26*, 589.
[20] Lee, D. W., Jin, J.-I., Laguerre, M., Achard, M. F., & Hardouin, F. (2000). *Liq. Cryst.*, *27*, 145.
[21] Mallia, V. A., & Tamaoki, N. (2003). *J. Mater. Chem.*, *13*, 219.
[22] Tamaoki, N., Aoki, Y., Moriyama, M., & Kidowaki, M. (2003). *Chem. Mater.*, *15*, 719.
[23] Lee, W.-K., Kim, K.-N., Achard, M. F., & Jin, J.-I. (2006). *J. Mater. Chem.*, 2289.
[24] Wu, C. C. (2007). *Mater. Lett.*, *61*, 1380.
[25] Marcelis, A. T. M., Koudijs, A., Klop, E. A., & Sudhölter, E. J. R. (2001). *Liq. Cryst.*, *28*, 881.
[26] Zhang, D. W., Huang, W., Pan, G. H., He, W. L., Cao, Y. B., Guo, J. B., Cao, H., & Yang, H. (2009). *Chem. Lett.*, *20*, 562.
[27] Yu, H. B., Huang, Z. G., Yin, B. Z., Jamil, M., & Jeon, Y. J. (2008). *Mater.Lett.*, *62*, 3284.
[28] Zhang, C. B., Jin, L. Y., Yin, B. Z., Jamil, M., & Jeon, Y. J. (2008). *Liq. Cryst.*, *35*, 39–44.
[29] Marcelis, A. T. M., Giesbers, M., & Koudijs, A. (2007). *Liq. Cryst.*, *34*, 811.
[30] Yelamaggad, C. V., Nagamani, S. A., Hiremath, U. S., Rao, D. S. S., & Prasad, S. K. (2001). *J. Chem. Res.*, *2001*, 493.
[31] Yelamaggad, C. V., Nagamani, S. A., Hiremath, U. S., Rao, D. S. S., & Prasad, S. K. (2001). *Liq. Cryst.*, *2001*, 493.
[32] Aldred, M. P., Hudson, R., Kitney, S. P., Vlachos, P., Lidetke, A., Woon, K. L., Neill, M. O., & Kelly, S. M. (2008). *Liq. Cryst.*, *35*, 413.
[33] Itahara, T., Sunose, M., Kameda, T., & Ueda, T. (2002). *Chem. Phys.*, *4*, 378.
[34] (a) Majumdar, K. C., Chakravorty, S., Pal, N., & Rao, N. V. S. (2009).*Tetrahedron*, *65*, 152; (b) Majumdar, K. C., Chattopadhyay, B., Chakravorty, S., Pal, N., & Sinha, R. K. (2008). *Tetrahedron Lett.*, *49*, 7149; (c) Majumdar, K. C., Pal, N., Debnath, P., & Rao, N. V. S. (2007). *Tetrahedron Lett.*, *48*, 6330; (d) Majumdar, K. C., Pal, N., Nath, S., Choudhary, S., & Rao, N. V. S. (2007). *Mol. Cryst. Liq. Cryst.*, *37*, 461; (e) Majumdar, K. C., Pal, N., & Rao, N. V. S. (2006). *Liq. Cryst.*, *33*, 531.
[35] Kim, K. N., Do, E-D., Kwon, Y-W., & Jin, J. (2010). *Liq. Cryst.*, *32*, 299.
[36] Lee, J. W., Park, Y. S., Jin, J.-I., Achard, M. F., & Hardouin, F. (2003). *J. Mater. Chem.*, *13*, 1367.
[37] Liu, H., & Nohira, H. (1997). *Liq. Cryst.*, *22*, 217.
[38] Wen, J., Chen, H., & Shen, Y. (1999). *Liq. Cryst.*, *26*, 1833.
[39] Wang, K., Li, H., & Wen, J. (2001). *J. Fluorine Chem.*, *109*, 205.
[40] Coates, D. (1995). Chemical structure, Molecular Engineering and Mixture Formulation, vol. 1. Chapter 3 In Behadur, B (Ed.). Liquid Crystals: Applications and uses. Singapore: Scientific Publishing Co. Pte. Ltd.