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Synthesis and Mesomorphic Behavior of Novel Calamitic Liquid Crystalline Dimesogens Possessing a Cholesteryl Moiety Connected to a Pyrimidine Core

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Novel non-symmetric dimesogens consisting of a cholesteryl moiety and a pyrimidine unit interconnected through a pentamethylene or decamethylene spacer have been prepared through palladium-mediated Sonogashira cross-coupling. The novel mesogens show only a chiral nematic phase. The liquid crystalline phase was investigated through polarizing optical microscopy and differential scanning calorimetry. All the compounds were characterized through elemental analyses and spectral data.

Keywords Calamitic liquid crystal; chiral nematic phase; cholesterol; dimesogens; pyrimidine

Dimesogenic compounds (twins), consisting of two different mesogenic units interlinked through a central spacer, are a relatively new class of liquid crystalline (LC) compounds that still require more intensive research in order to establish the relationship between their structure and LC properties [1–23]. The non-symmetrical dimers are markedly different from symmetrical ones as they exhibit interesting polymorphic sequence [24, 25] and stabilize wide-range chiral nematic (N*) mesophases [26]. Due to commercial availability of cholesterol as an inexpensive natural product, its rigid structure with eight chiral centers and the ease with which the structure can be derivatized, it has been incorporated extensively in chiral LC materials. The ability of cholesterol in inducing an LC property in its various derivatives motivated many researchers to synthesize thousands of monomers, oligomers, and polymers derived from cholesterol[27, 28]. Non-symmetric dimers derived from naturally occurring cholesterol represent an exemplary and emerging class of chiral liquid crystals. In general, cholesterol dimers contain cholesterol moiety and another mesogen, such as a Schiff's base [29] and an azobenzene [30, 31], stilbene [32], or tolane [33] unit.

Uracil is found in various natural products and has numerous applications in organic synthesis [34]. However, some unsuccessful attempts [35–37] have been made to prepare thermotropic liquid crystals of nucleobase. Itahara et al. [38] reported on the LC materials formed by connecting adenine or thymine to cholesteryl benzoate or related steroid groups through a polymethylene spacer. Their results suggested that base pairing plays an important role in the control of LC properties. There are also few reports regarding the formation of

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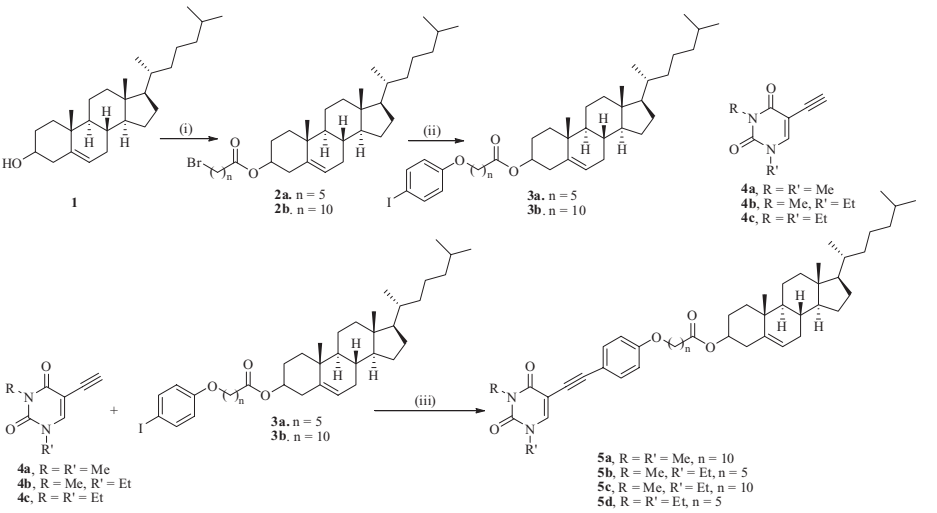
lyotropic liquid crystals by DNA and nucleotides [39, 40]. In continuation to our ongoing research on the synthesis of LC materials containing heterocyclic cores [41–55] we became interested to synthesize uracil containing non-symmetrical dimesogens and in our recent investigations [46, 47] we had demonstrated that when uracil is connected to a cholesteryl moiety through C=N or C=C linkage, it exhibits a twist grain boundary (TGB) phase over a wide temperature range along with a chiral nematic and smectic phases. Being inspired by our results and for understanding the structure-LC property relationship, we have undertaken a study on the synthesis and characterization of new dimesogenic compounds containing uracil moiety connected to a cholesteryl moiety through a tolane linkage. Herein we report our results.

2. Results and Discussions

The synthetic route for A new class of calamitic liquid crystals (**5a–d**) is depicted in Scheme 1. The required precursors **3a**,**b** were synthesized from naturally occurring cholesterol. Esterification of cholesterol (**1**) with the bromoalkanoylchlorides was carried out in tetrahydrofuran (THF) in the presence of pyridine to afford **2a**,**b** compounds. The cholesteryl 4-iodo alkyl esters (**3a**,**b**) were prepared [56] by the reaction of compounds **2a**,**b** with 4-iodophenol in refluxing acetone in the presence of anhydrous K_2CO_3 (Scheme 1). The other precursors **4a–c** were synthesized following a standard literature procedure [57, 58]. Finally, the target compounds (**5a–d**) were successfully obtained by Sonogashira coupling between compounds **3a**,**b** and **4a–c** by using $Pd(PPh_3)_2Cl_2$ (10 mol%) as catalyst, CuI (10 mol%) as co-catalyst, and triethyl amine as base in THF. The compounds were characterized from their elemental analysis and spectral data.

2.1. Mesomorphic Properties

The mesomorphism of compounds **5a–d** is characterized and studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). With a view to



Scheme 1. Reagents and conditions: (i) Bromoalkanoyl chloride, THF, pyridine, rt, 12 h; (ii) p-iodo phenol, acetone, K_2CO_3, reflux, 12 h; (iii) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, THF, rt, 12 h.

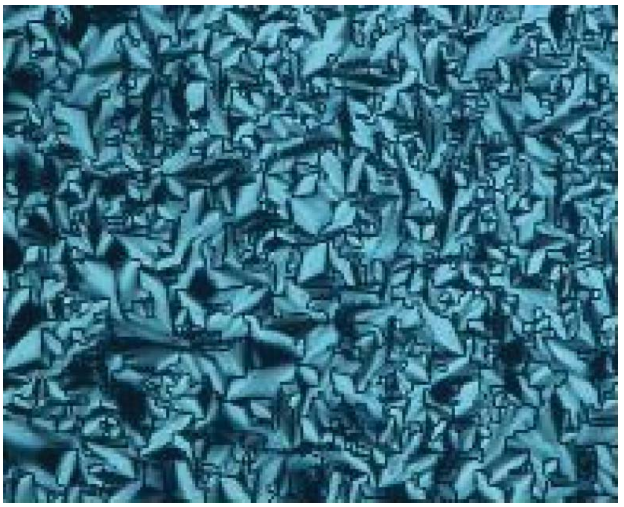


Figure 1. Compound **5b** at 112°C.

understanding the relationship between the structure and mesomorphic properties in calamitic pyrimidine derivatives, we have synthesized a series of compounds **5a–d** in which we systematically changed the spacing of the carbon chain on the cholesteryl moiety (n = 5, 10) and the alkyl group in the pyrimidine moiety.

All the mesogenic compounds showed phase sequence of crystal-N*-isotropic. For the compounds having the same *N*-alkyl groups, the melting as well as clearing temperatures decreases with increase in the spacer length of the cholesteryl moiety. When undecamethylene spacer of **5a** was replaced by a hexamethylene spacer, compound **5b** also displayed the same phase sequence (Fig. 1) only with increase in the isotropic temperature. All the other compounds exhibit similar type of phase behavior under POM observation (Fig. 2).

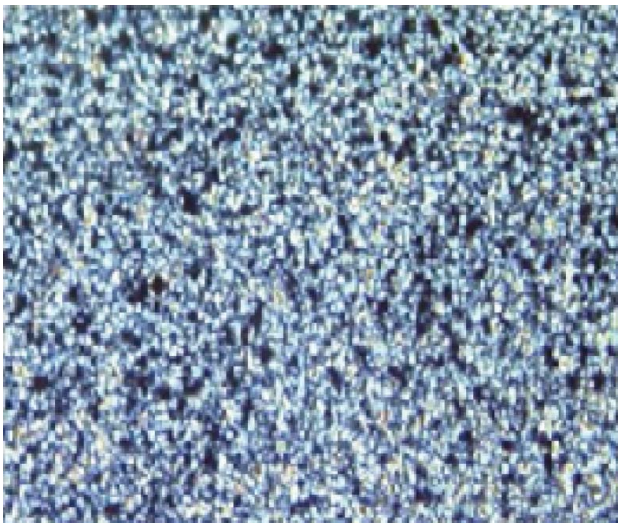


Figure 2. Compound **5c** at 88°C.

Table 1. Transition temperatures (°C)[a] and associated enthalpies (KJ/mol) of unsymmetrical LC dimesogens

Dimers	Heating cycle	Cooling cycle
5a	Cr 104.5 (0.1) N*	I105.6 (2.8) N*
	115.4 (22.7) I	90.8 (0.01) Cr
5b	Cr 128.4 (0.03) Cr_1	I 121.4 (3.6) N*
	135.0 (0.03) N*	100.5 (15.9) Cr
	155.0 (40.9) I	
5c	Cr 108.1 (20.0) N*	I 91.0 (0.01) N*
	128.6 (0.1) I	80.0 (2.7) Cr
5d	Cr 90.4 (0.1) N*	I 137.7 (0.01) N*
	151.0 (39.4) I	88.1 (0.9) Cr

[a]Peark temperatures in the DSC thermograms obtained during the first heating and cooling cycles at 5°C min^{-1}. I: isotropic liquid state; N*: chiral nematic; Cr and Cr_1: crystals.

The phase transition temperatures and associated enthalpies are summarized in Table 1. All the compounds exhibit only two transitions in both heating and cooling cycles except **5b**, which exhibits an additional transition in the heating cycle, probably due to a solid–solid transformation. For all the compounds of the series, the enthalpy change across the crystal to mesophase transition is much smaller than that for the mesophase to isotropic phase transition in the heating mode, and while considering the cooling cycle, except compound **5a**, for all the other dimers the enthalpy change across the isotropic phase to mesophase transition is much smaller than that for the mesophase to crystal transition.

2.2. Optical Properties

The UV-Vis absorption and fluorescence spectra of the compounds **5a–d** in $CHCl_3$ solution are shown in Figs. 3 and 4(a), (b) respectively. The absorption and emission spectra of

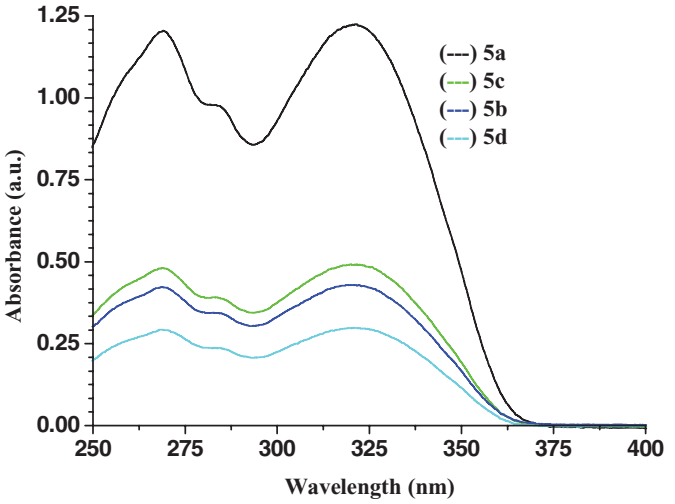
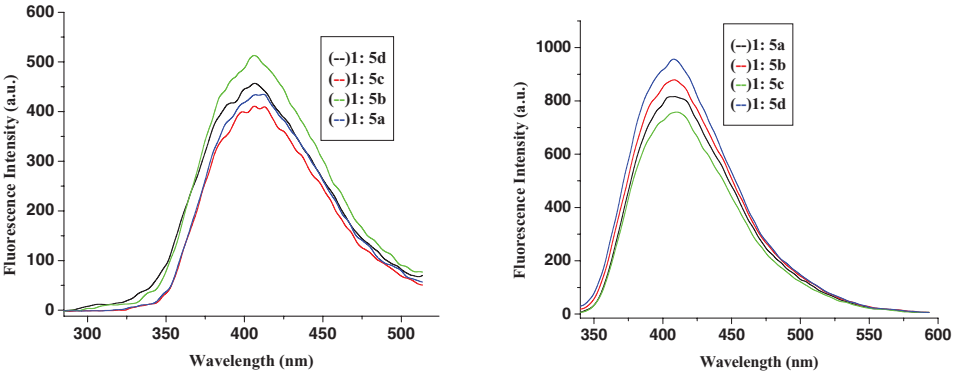


Figure 3. UV-Vis spectra of compounds **5a–d** in $CHCl_3$.



(a) (b)

Figure 4. (a) Fluorescence spectra of compounds **5a-d** in $CHCl_3$ (excitation at 268 nm). (b) Fluorescence spectra of compounds **5a-d** in $CHCl_3$ (excitation at 321 nm).

all the compounds **5a–d** are very similar in shape due to their structural similarity. The absorption peaks of all the compounds are found to be near about 268 nm and 321 nm. The absorbance is maximum for compounds **5a**, and for compound **5d** it is at a minimum. For compounds having similar *N*-alkyl groups, absorbance decreases with decrease in spacer length. In order to record the fluorescence spectra, we excited the compounds at 268 nm and 321 nm. In case of fluorescence spectra, the emission peaks occurred at around 407 nm and 409 nm for all the compounds irrespective of the spacer length. Fluorescence intensity was found to be at a maximum for compound **5b** on excitation at 268 nm. Compound **5d** exhibited maximum intensity on excitation at 321 nm.

Itahara et al. [38] explained the thermotropic behavior of their mesogenic compounds containing adenine and thymine moiety by considering Watson–Crick base pairing (intermolecular H-bonding). However, in our present instance, the compounds cannot form Watson–Crick base pairing or similar hydrogen bonds.

3. Conclusion

In summary, we have reported the synthesis and characterization of novel calamitic dimesogens, in which a pyrimidine unit is covalently tethered to a bulky chiral rod-like mesogen through a tolane linkage. The dimesogenic compounds show only a chiral nematic phase irrespective of the spacer length or the *N*-alkyl groups. Such a molecular design favors formation of nematic phase over a reasonable thermal range.

4. Experimental

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 **thin layer chromatography** (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. UV and fluorescence spectra were recorded in $CHCl_3$ on a Shimadzu UV-2401PC spectrophotometer (λ_{max} in nm). ^1H NMR and ^{13}C NMR (400 MHz, 500 MHz) spectra were recorded on a

Bruker DPX-400, DPX-500 spectrometer in $CDCl_3$ (chemical shift in δ) with tetramethylsilane (TMS) as internal standard. The LC properties were established through thermal microscopy (Nikon polarizing microscope LV100POL attached to Instec hot and cold stage HCS302, with STC200 temperature controller configured for HCS302), and the phase transitions were confirmed (both heating and cooling rate is 5° min^{-1}) by differential scanning calorimetry (Perkin–Elmer DSC Pyris1 system). The HRXRD was carried out at Centre for Soft Matter Research (CSMR), Bangalore, India by employing PAN analytical X'Pert PRO diffractometer equipped with a high-resolution, fast detector PIXCEL.

General procedure for the synthesis of compounds 3a,b:

Compounds **3a,b** were prepared according to the previously published procedures [56].

General procedure for the synthesis of compounds 4a–c:

Compounds **4a–c** were prepared according to the previously published procedures [57, 58].

General procedure for the synthesis of compounds 5a–d:

Nitrogen gas was purged through a solution of compound **4a** (100 mg, 0.61 mmol), **3b** (566 mg, 0.732 mmol), and Et_3N (4 mL) in dry THF (10 mL) for 30 min. Then catalyst $Pd(PPh_3)_2Cl_2$ (42.8 mg, 0.061 mmol) and co-catalyst CuI (11.6 mg, 0.061 mmol) were added and stirred for 12 h at room temperature. THF was removed followed by extraction with $CHCl_3$ (3×30 mL), and the extract was washed with H_2O (2×20 mL) followed by brine (10 mL) and dried Na_2SO_4, and the solvent was evaporated to give crude product, which was purified by column chromatography over silica gel by EA:PE (1:19) as eluant to afford compound **5a**. Compounds **5b–d** were prepared with similar procedure.

Compound 5a: White solid, yield 92%, IR (KBr): 2933, 1735, 1711, 1695, 1656, 1602 cm^{-1}, ^1H NMR (400 MHz, $CDCl_3$): $\delta_H = 7.49$ (s, 1H), 7.42 (d, 2H, $J = 8.4$ Hz), 6.84 (d, 2H, $J = 8.8$ Hz), 5.38 (s, 1H), 4.60–4.62 (m, 1H), 3.95 (t, 2H, $J = 6.8$ Hz), 3.45 (s, 3H), 3.40 (s, 3H), 2.25–2.32 (m, 4H), 0.86–2.02 (m, 54H), 0.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 161.8, 159.4, 150.9, 144.7, 139.7, 133.1, 122.6, 114.5, 99.6, 93.5, 79.0, 73.7, 68.1, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.3, 37.0, 36.6, 36.2, 35.8, 34.7, 31.90, 31.86, 29.5, 29.3, 29.23, 29.17, 29.1, 28.4, 28.2, 28.0, 27.8, 26.0, 25.1, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.9; Anal. Calcd. for $C_{52}H_{76}N_2O_5$: C, 77.18; H, 9.47; N, 3.46%. Found: C, 77.16; H, 9.46; N, 3.49%.

Compound 5b: White solid, yield 91%, IR (KBr): 2947, 1737, 1721, 1698, 1655, 1602 cm^{-1}, ^1H NMR (500 MHz, $CDCl_3$): $\delta_H = 7.49$ (s, 1H), 7.42 (d, 2H, $J = 8.4$ Hz), 6.83 (d, 2H, $J = 8.8$ Hz), 5.37 (d, 1H, $J = 4.4$ Hz), 4.61–4.63 (m, 1H), 3.96 (t, 2H, $J = 6.4$ Hz), 3.86 (q, 2H, $J = 7.2$ Hz), 3.39 (s, 3H), 2.31 (t, 4H, $J = 7.5$ Hz), 0.86–2.02 (m, 47H), 0.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.0, 161.8, 159.3, 150.5, 143.7, 139.7, 133.1, 122.6, 114.6, 114.4, 99.7, 93.4, 79.2, 73.8, 67.7, 56.7, 56.1, 50.0, 45.4, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.5, 31.90, 31.86, 29.7, 28.9, 28.4, 28.2, 28.0, 27.8, 25.6, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 14.5, 11.9; Anal. Calcd. for $C_{48}H_{68}N_2O_5$: C, 76.56; H, 9.10; N, 3.72%. Found: C, 76.50; H, 9.16; N, 3.79%.

Compound 5c: White solid, yield 90%, IR (KBr): 2932, 1732, 1713, 1660, 1647, 1604 cm^{-1}, ^1H NMR (500 MHz, $CDCl_3$): $\delta_H = 7.49$ (s, 1H), 7.42 (d, 2H, $J = 8.8$ Hz), 6.84 (d, 2H, $J = 8.8$ Hz), 5.37 (d, 1H, $J = 4.7$ Hz), 4.60–4.62 (m, 1H), 3.95 (t, 2H, $J = 6.6$ Hz), 3.86 (q, 2H, $J = 7.2$ Hz), 3.39 (s, 3H), 2.25–2.32 (m, 4H), 0.86–2.02 (m, 57H), 0.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 161.8, 159.4, 150.5, 143.7, 139.7, 133.1, 122.6, 114.5, 99.7, 93.4, 79.2, 73.7, 68.0, 56.7, 56.1, 50.0, 45.4, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 34.7, 31.90, 31.85, 29.7, 29.5, 29.3, 29.2, 29.1, 28.4, 28.2, 28.0, 27.8, 26.0, 25.1, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 14.5, 11.9; Anal. Calcd. for $C_{53}H_{78}N_2O_5$: C, 77.33; H, 9.55; N, 3.40%. Found: C, 77.46; H, 9.56; N, 3.49%.

Compound 5d: White solid, yield 84%, IR (KBr): 2951, 1730, 1707, 1655, 1645, 1602 cm^{-1}, ^1H NMR (500 MHz, $CDCl_3$): $\delta_H = 7.48$ (s, 1H), 7.43 (d, 2H, $J = 8.8$ Hz), 6.83 (d, 2H, $J = 8.8$ Hz), 5.38 (s, 1H), 4.61–4.63 (m, 1H), 4.06 (q, 2H, $J = 7.2$ Hz), 3.96 (t, 2H, $J = 6.4$ Hz), 3.85 (q, 2H, $J = 7.2$ Hz), 2.32 (t, 4H, $J = 7.2$ Hz), 0.85–2.02 (m, 50H), 0.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 173.0, 161.8, 159.4, 150.5, 143.7, 139.7, 133.1, 122.5, 114.6, 99.7, 93.4, 79.2, 73.7, 68.0, 56.7, 56.1, 50.0, 45.4, 42.3, 39.7, 39.4, 38.2, 37.0, 36.6, 36.2, 35.8, 34.7, 31.90, 31.85, 29.7, 29.5, 29.4, 29.2, 29.1, 28.4, 28.2, 28.0, 27.8, 26.0, 25.1, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 14.5, 13.8, 11.9; Anal. Calcd. for $C_{49}H_{70}N_2O_5$: C, 76.72; H, 9.20; N, 3.65%. Found: C, 76.76; H, 9.46; N, 3.71%.

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