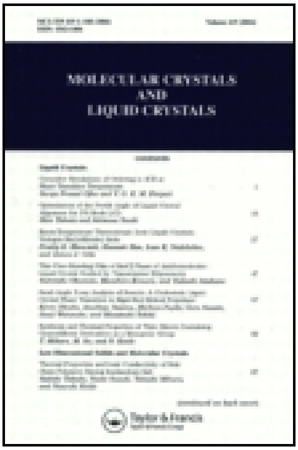

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Study of Chiral Dimesogens: Liquid Crystalline Properties, Effect of Smectic Cybotactic Domains in Controlling the Chiral Reflections and Glassy Liquid Crystal Forming Properties

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Liquid crystalline properties, temperature dependent reflection studies and glassy liquid crystal forming properties of azobenzene/alkylazobenzene containing cholesterol dimesogens with varying methylene spacers have been described. All these compounds exhibit chiral nematic phases, and both chiral nematic and smecticA phases have been observed for the dimesogens containing 4-alkylazobenzene moieties. X-ray diffraction studies in the smecticA phases of these dimesogens show that both monolayer and intercalated arrangements co-exist in the meso phase. Selective reflection observed in the chiral nematics was found to be red shifted upon lowering the temperature due to fluctuations in smectic order. By rapid cooling of the 4-alkylazobenzene compounds from the cholesteric phase transition temperature to 0°C, solid films maintaining a helical molecular order were obtained.

Keywords: chiral dimesogens; glassy liquid crystals; selective reflection; smectic cybotactics

INTRODUCTION

Liquid crystalline (LC) materials are widely used for display devices because their flexible ordered structures can lead to systems displaying switchable optical modulation. Dimesogens/dimers/twins (LCs containing two mesogenic units linked through a flexible spacer) are attracting much attention these years because they exhibit new LC

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phases, serve as useful models for semi-flexible, main chain LC polymers and show unique properties applicable for new optical materials [1–3]. Cholesteric liquid crystals (ChLCs) continue to attract a great deal of attention because their unique helical structures give rise to selective reflection of the incident light satisfying the relationship $\lambda = \mathrm{np}$, where n is the average refractive index of the LC material and p is the helical pitch [4–14]. Hardouin, Jin and co workers reported on the frustrated phases in unsymmetrical dimesogenic materials [15–20]. Frustrated LC phases arise due to the competition between two mesogenic parts, which also depends on the length of flexible linkages. In this report, LC properties, temperature dependent reflection studies and glassy LC forming properties of azobenzene/alkylazobenzene containing cholesterol dimesogens with varying methylene spacers have been described (Chart 1).

In unsymmetric dimesogenic systems constituting chemically different mesogenic groups linked together by a flexible spacer, two kinds of smectic modulations are generally observed. One corresponds to a layer spacing that is approximately half of the molecular length (intercalated structure), while the other corresponds to a layer spacing that is nearer to or greater than the molecular length. Formation of these smectic modulations entirely depends on the length of the methylene spacer present in the molecule. In general when flexible chain length is small monolayer arrangement is stabilized and for the higher flexible chains intercalated arrangement is observed. For intermediate molecular lengths, co-existence of both the periodicities are seen. Reports on incommensurate phases as well as two-dimensional ribbon phases are also available in the literature. This paper also describes the change in the ratio of the two co-existing smecticA arrangements with temperature in dimesogen **7n7**, which was systematically studied using x-ray diffraction (XRD) studies.

EXPERIMENTAL SECTION

The high-resolution proton NMR spectra of all the intermediates and the final compounds were recorded using a Varian (300 MHz) spectrometer using $CDCl_3$ as the solvent. The optical textures of the mesophases were observed and identified using a polarizing optical microscope (Olympus BX 60) equipped with a hot stage (Mettler, FP82 or FP 90). Both electronic absorbance and reflection spectra were recorded on UV-Vis spectrophotometers (Hewlett-Packard 8453 and Otsuka Electronics MCPD-1000 respectively) The phases observed under polarizing microscope was also confirmed using a differential scanning calorimeter (Seiko instrument DSC 5200). XRD patterns were obtained using a Rigaku diffractometer (Type 4037) with type graded d-space elliptical side-by-side multilayer optics, monochromated Cu Kα (40 kV, 30 mA), and imaging plate (R-axis IV). The samples were contained in quartz capillary tubes (1.5-mm diameter, 0.01 mm wall thickness) and positioned on a hot stage. The samples were heated to their isotropic state, subsequently cooled in to the mesophases, and then exposed to a radiation beam for 30 s. Samples of the mixtures in the cholesteric LC phase were prepared by sandwiching the uniform mixture between two glass or quartz plates with temperature control using a hot stage (Mettler, FP 82 or FP 90).

MATERIALS

The dimesogens investigated in the present study were prepared as described in the synthesis of related compounds [21,22]. These compounds were characterized based on the analytical and spectral data as illustrated below.

n3: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.67–2.20 (m) 2.58 (2H, t), 4.60 (1H, m), 5.37 (1H, m), 7.25 (2H, d), 7.49–7.52 (3H, m), 7.92 (2H, d), 7.94 (2H, d). Anal. Calcd for $C_{44}H_{60}N_2O_4$: C, 77.61; H, 8.88; N, 4.11. Found C, 77.80; H, 8.86; N, 4.07.

n5: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.67–2.20 (m) 2.56 (2H, t), 4.62 (1H, m), 5.37 (1H, m), 7.24 (2H, d), 7.49–7.51 (3H, m), 7.90 (2H, d), 7.94 (2H, d). Anal. Calcd for $C_{46}H_{64}N_2O_4$: C, 77.92; H, 9.10; N, 3.95. Found C, 78.33; H, 9.10; N, 3.78.

4n7: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.66–2.20 (m), 2.58 (2H, t), 2.69 (2H, t), 4.65 (1H, m), 5.39 (1H, m), 7.22 (2H, d), 7.31 (2H, d), 7.82 (2H, d), 7.93 (2H, d). Anal. Calcd for $C_{52}H_{76}N_2O_4$: C, 78.74; H, 9.66; N, 3.53. Found C, 78.63; H, 9.58; N, 3.50.

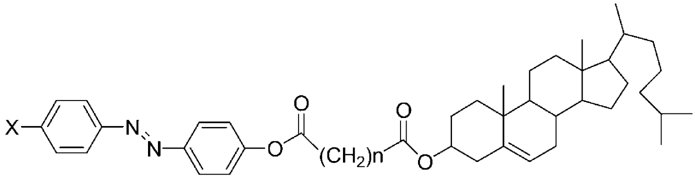
7n7: ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.66–2.20 (m), 2.57 (2H, t), 2.69 (2H, t), 4.64 (1H, m), 5.39 (1H, m), 7.22 (2H, d), 7.30 (2H, d), 7.82 (2H, d), 7.93 (2H, d). Anal. Calcd for $C_{55}H_{82}N_2O_4$: C, 79.09; H, 9.90; N, 3.35. Found C, 78.72; H, 10.18; N, 3.32.

Preparation of cholesteric glassy liquid crystals (GLC): A powdered sample sandwiched between two thin glass plates ($20 \times 20 \times 0.18$ mm) was placed on a hot stage and heated to the cholesteric temperature. The sample was rapidly quenched by dipping into ice water to obtain a cholesteric glassy liquid crystalline film.

RESULTS AND DISCUSSION

Mesomorphic Properties

We have earlier reported on the LC properties of a series of chiral dimesogenic compounds containing cholesteryl/azobenzene moieties



n3, X=H, n =3
n5, X=H, n=5
n7, X=H, n=7
4n7, X= C_4H_9, n=7
7n7, X= C_7H_{15}, n=7

CHART 1 Investigated dimesogens.

linked to varying alkyl chain lengths (6–14) [21]. In this series all compounds except the dimesogen containing 7 methylene spacers (**n7**) show a chiral nematic phase. Compound **n7** exhibit a short-range smecticA phase and the d/L ratio was observed to be 1.2, where d is interlayer distance obtained from x-ray studies and L is the molecular length [22]. To study more details on the effect of flexible chain and LC properties we have synthesized **n5** and **n3** (Chart 1). The dimesogen containing 5 methylene spacers (**n5**) exhibits a monotropic meso phase from 114°C to 108°C. Both the fingerprint texture and the single color reflecting Grandjean texture exhibited in this compound confirm the formation of a ChLC phase. Similarly the dimesogen **n3** also exhibit a monotropic chiral nematic phase from 113.9°C to 94.4°C.

The dimesogen **4n7**, which contains the 4-butylazobenzene group, undergoes a crystalline-to chiral nematic (N^*) at 127.4°C before changing to the isotropic phase at 147.6°C during the heating cycle. In the cooling cycle the N^* phase is transformed to a monotropic smecticA phase. The dimesogenic compound **7n7** show a SmA^* phase and a N^* phase. Phase transition temperatures as well as enthalpy changes obtained for the dimesogens are summarized in Table 1.

X-ray Diffraction Studies

For further verification of the smectic LC phases, x-ray diffraction studies have been carried out. The XRD pattern of **4n7** shows two reflections at small angle and a diffuse peak in the wide-angle region. The inter-layer distances calculated from XRD for **4n7** 20.8 ($d/L = 0.49$) and 38.3 ($d/L = 0.9$) Å (Fig. 1). This can be explained by assuming the

TABLE 1 Phase Transition Temperatures and Enthalpies of the Dimesogens

	Phase transition temperature/°C^{a,b} (ΔH/kJ mol^{-1})	
	Heating	Cooling
n3	Cr 116.9 (27.4) Iso	Iso 113.9 (0.3) N* 94.4 (29.4) Cr
n5	Cr 128.5 (26.1) Iso	Iso 114.4 (0.2) N* 108.0 (27.2) Cr
n7	Cr 110.6 (23.4) SmA* 114.9 (0.13) Iso	Iso 112.6 (0.6) SmA* 95.5 (31.5) Cr
4n7	Cr 127.4 (38.8) N* 147.6 (1.1) Iso	Iso 145.1 (0.8) N* 98.4 SmA* 85.5 (33.7) Cr
7n7	Cr 122.7^{c} SmA* 125.4 N* 145.7 (1.3) Iso	Iso 141.6 (1.3) N* 106.3 SmA* 58.5 (26.6) Cr

[a] Transition temperatures are obtained from DSC analysis at a rate of 5°C min^{-1} in the first heating and cooling cycles.

[b] Cr = crystalline, N* = cholesteric, SmA* = smecticA and Iso = Isotropic.

[c] Observed from polarizing optical microscope.

formation of intercalated (d/L = 0.49) and monolayer (d/L = 0.9) type arrangements. The observed wide-angle reflection could be due to the liquid like order in the smectic layers. Coexistense of multiple periodicities has been observed for other non-symmetric dimesogens [19,23].

The dimesogen **7n7** also exhibit two sharp reflections at lower angle and a broad reflection at wide angle. For the dimesogenic compounds,

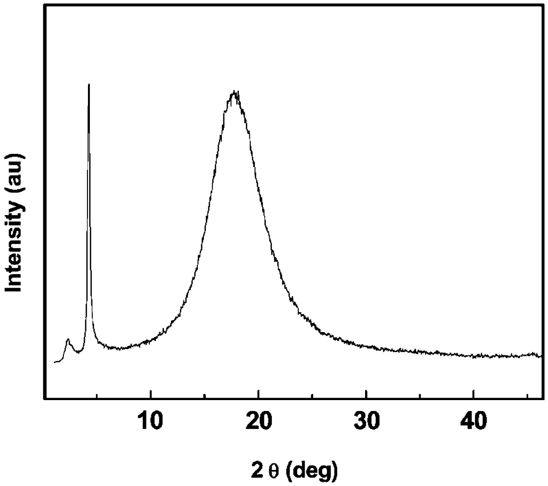


FIGURE 1 The intensity profiles of the x-ray diffraction pattern exhibited by **4n7** at 98°C (cooling cycle).

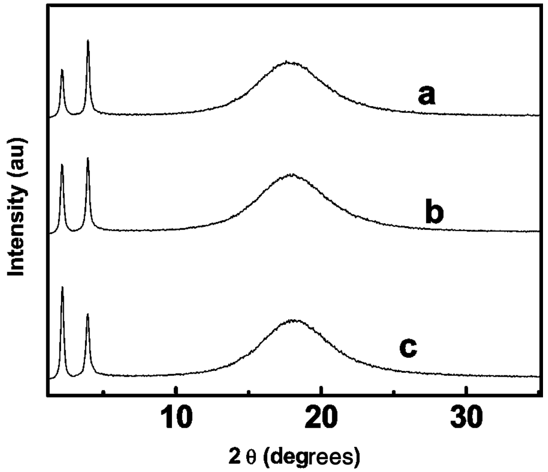
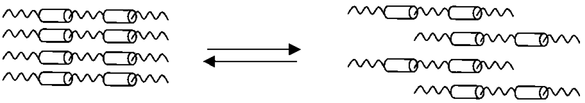


FIGURE 2 The intensity profiles of the x-ray diffraction pattern exhibited by **7n7** at different temperatures a) 115°C, b) 105°C and c) 90°C (cooling cycle).

monolayer and intercalated arrangements occur quite commonly and generally depend on the length of methylene spacer. The temperature-dependent x-ray diffraction studies for **7n7** show that upon lowering the temperature, the ratio of the monolayer-to-intercalated layer arrangements shifts more towards monolayer arrangement (Fig. 2). Alternatively as the temperature increases the dimesogens become more flexible and the layer arrangement changes to an intercalated form (Scheme 1).

Effect of Temperature on the Cholesteric Pitch

The molecular ordering of ChLCs in a helical arrangement induces reflection at the wavelength satisfying the equation $\lambda_{\max} = \mathrm{np}$, where $\lambda_{\max}$ is the reflection maximum, n is the average refractive index and p is the pitch of the helix. The pitch length of a cholesteric LC can increase or decrease with temperature depending on the sign of the thermal coefficient α, which is equal to $1/p\ [dp/dT]$, where p is the



SCHEME 1 Representation of the change in molecular arrangement observed in **7n7** in the SmA* phase.

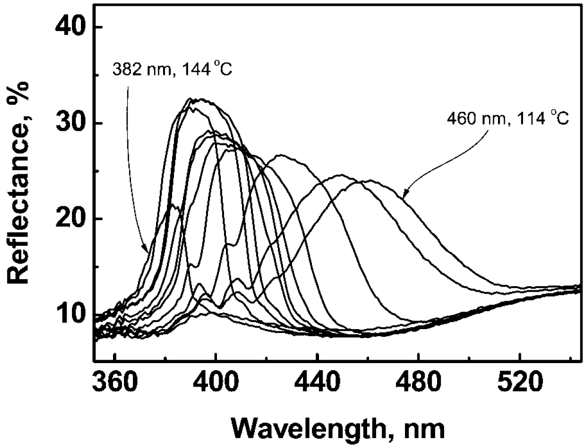


FIGURE 3 Reflectance spectra of **7n7** at different temperatures.

pitch length and T is the temperature. When [dp/dT] >0 pitch length will increase with increasing temperature and vice versa. In the present study it has been found that [dp/dT]<0. The dimesogen **4n7** exhibit a reflection band at 388 nm at 146°C, and the reflection band is red-shifted to 443 nm upon cooling to 104°C. In the case of **7n7**, a wavelength shift of 78 nm was observed. Upon cooling from 144°C to 114°C the $\lambda_{\max}$ shifted from 382 nm to 460 nm (Fig. 3).

Our earlier research on dimesogens show that compounds with an odd number of carbon atoms in the spacer have a slightly distorted rod shape [21]. This structure destabilizes the formation of smectic cybotactic groups (smectic fluctuations) even at low temperatures. In dimesogenic compounds containing cholesteryl/azobenzene moieties linked to varying odd alkyl chain lengths (9, 11 and 13), the observed wavelength shift of the selective reflected band was 12 nm. The increased the wavelength shift of the selective reflection band with temperature in present systems containing, alkyl substitution on the azobenzene could be explained by the effect of smectic cybotactic groups present in the cholesteric moiety. These cybotactic groups both restrict helical twisting and increase the wavelength shift due to the smectogenic property of dialkyl azobenzene moiety [21]. To explore the mechanism responsible for the shift in the reflection wavelength for the compound **7n7**, small-angle X-ray diffractometric studies were carried out at different temperatures in the N* phase. Figure 4 show the X-ray diffractograms obtained for **7n7** at different temperatures during the cooling cycle. The X-ray diffractogram of **7n7** in the

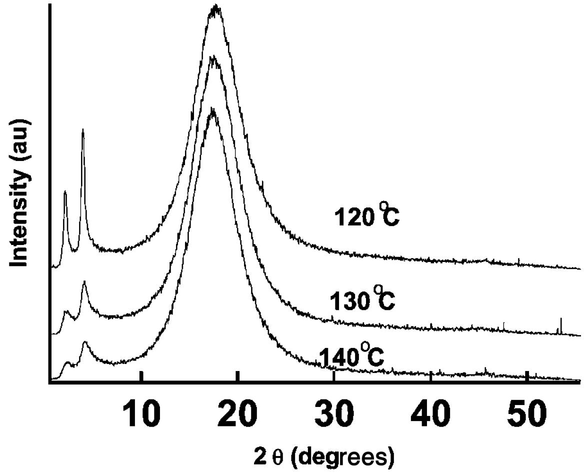


FIGURE 4 The intensity profiles of the x-ray diffraction pattern exhibited by **7n7** at different temperatures (cooling cycle).

cholesteric phase show low intensity reflections (smectic fluctuations or smectic cybotactic groups) at small angles. As the cholesteric phase is cooled the smectic fluctuations become more pronounced leading to sharpening of the small-angle peak. These studies suggest that the mechanism for the change in reflection wavelength observed in the dimesogen **7n7** could be due to variations in the smectic cybotactic groups.

Glassy Cholesteric Liquid Crystal

Glassy LCs (GLCs) constitutes a state of matter wherein the long-range molecular order of LC is frozen in an “amorphous” solid state. The compounds **4n7** and **7n7** were solidified while maintaining the LC molecular order by rapidly cooling the LC phase (see the experimental section for details of GLC preparation). Upon heating, cholesteric GLCs changed to crystalline at certain temperature. Stability of these GLCs were examined using DSC. Figure 5 show DSC thermogram obtained for the cholesteric GLC of **4n7**.

Second order transitions, which are indicated by steps in the DSC thermograms, were not observed in these compounds. These results indicate that the exotherms observed in the heating cycle of the DSC thermograms denote a phase change sequence from GLC to the “fluid” cholesteric phase, followd by recrystallization to the solid state. This phase sequence was also confirmed using a temperature

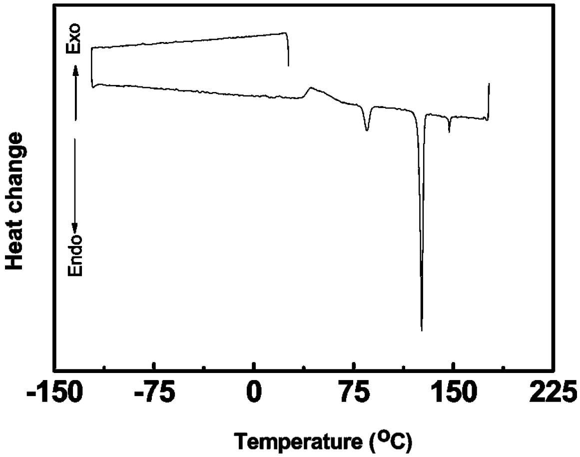


FIGURE 5 DSC thermogram of **4n7** on heating from the glassy liquid crystal obtained upon sudden cooling from 120°C.

controlled hot stage, which visually showed the crystallization of cholesteric GLCs). For example, the GLC phase obtained by sudden cooling of **4n7** and **7n7** from 120°C exhibit a cholesteric GLC to crystal transition temperature at 44°C and 41°C respectively.

CONCLUSION

Azobenzene and cholesterol containing dimesogenic materials showing liquid crystalline properties have been synthesized and characterized. X-ray studies show that the dimesogens **4n7** and **7n7** exhibit coexistence of intercalated and monolayer arrangements in their SmA* phase. In **7n7** the ratios of the multiple periodicities have shown to be varied with temperature. X-ray diffraction studies of **7n7** in cholesteric liquid crystalline phase confirm the shift in reflected wavelength on change in temperature is due to the variations in smectic fluctuations. By rapid cooling the dimesogens **7n7** and **4n7** from the cholestric temperature to the 0°C glassy liquid crystalline film maintaining a cholesteric molecular order were obtained.

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