

## Photo-Thermal Effects of Some Cholesterol-Azobenzene Containing Dimesogens

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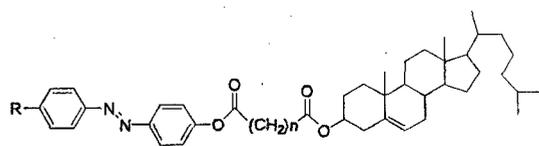
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Photo and temperature effects of cholesteric reflected wavelengths in some inherently photoresponsive cholesterol-azobenzene containing dimesogens have been described. These molecules exhibit cholesteric liquid crystalline phases and the reflected wavelengths have been observed at the visible region. The reflected wavelength shifts to red region upon cooling these dimesogens. Shift in the reflected wavelengths can also be obtained by the irradiation of these dimesogens at 366 nm. Formation of small amount of cis isomer of azo group hypsochromically shifts the wavelength. Upon irradiation of the dimesogen having heptylene spacer in between cholesteryl and azobenzene groups and heptylene linker on the para position of azobenzene group exhibit a smectic to cholesteric photoinduce phase transition.

Key words: Dimesogen, cholesteric liquid crystal, photoswitching, phase transition

### 1. INTRODUCTION

Recently dimesogens/liquid crystal dimers are getting considerable attraction because of their unique behavior compare to other conventional low molecular mass liquid crystals.<sup>[1,2]</sup> Many of the studies are regarding the formation of novel liquid crystalline phases from the dimesogenic materials and also their structure-property relation. It has been also reported that dimesogenic materials could serve as a useful model compounds for polymers. Our interest in this area has been concerned with the designing of some novel materials with dimesogens which can be useful in photonics as well as information technology.<sup>[3,4]</sup> Dimesogens can be considered as the lowest possible oligomer and exhibit some characteristic properties of polymers such as glass formation. Glassy liquid crystals are materials, which constitute a state of matter wherein the long-range molecular order of liquid crystals is frozen into the solid state. The combination of optical properties of liquid crystals and mechanical properties of solids makes glassy liquid crystals exclusively suited for variety of practical applications.<sup>[5]</sup> Earlier work from our group has shown that dimesogenic materials are suitable candidates for this function. Another important aspect of dimesogenic materials is that, we can tune the property of the materials by substituting two different mesogenic groups as well as linking with different flexible chains. This work deals with the photo-thermal change in the helical superstructures of a series of dimesogenic compounds containing cholesterol-azobenzene groups linked with alkyl chain (Chart 1).<sup>[6]</sup> Photostimulated modulation between smectic A and cholesteric phases have been also described using the dimesogen containing  $n = 7$  and  $R = C_7H_{15}$ .<sup>[6]</sup>



**n6, n7 to n14**, where  $n = 6, 7$  to  $14$  and  $R = H$

**7n7**,  $n = 7$  and  $R = C_7H_{15}$

Chart 1

### 2. EXPERIMENTAL

Reagent grade reactants and solvents were used as received from suppliers. Spectroscopic grade solvents were used for all measurements. Phase transitions were observed using a polarized light microscope (Olympus BX60) equipped with a hot stage (Mettler, FP82 and FP90). Differential scanning calorimetric studies were performed using a Seiko Instrument SSC5200. X-ray diffraction patterns were measured using a Rigaku diffractometer (Type 4037) with graded d-space elliptical side-by-side multilayer optics, monochromated Cu K $\alpha$  radiation (40 kV, 30 mA) and imaging plate (R-Axis IV). The samples were put 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 phase, subsequently cooled to the mesophase and then exposed radiation beam for 30 s with a 150 mm camera length. Electronic and reflection spectra were recorded on UV-Vis spectrophotometers (Agilent 8453 and Otsuka Electronics MCPD-1000 respectively). Steady state photo irradiation experiments were carried out using a high-pressure mercury lamp (500 W, Ushio) using appropriate glass filters (366 nm: Toshiba Glass Co., UV-35 + UVD-36C). The dimesogens containing azobenzene/cholesterol investigated in the present study were prepared as described in the synthesis of related compounds.<sup>[7,8]</sup> These compounds were characterized based on the analytical and spectral data.

### 3. RESULTS AND DISCUSSION

#### 3.1. Liquid Crystalline Properties

The mesomorphic properties of the dimesogens were investigated using polarizing optical microscopy (POM) as well as by small angled x-ray diffractometry and the phase transition temperatures were confirmed by differential scanning calorimetry (DSC). The fingerprint and single color reflecting Grandjean textures exhibited in this compound confirms the formation of a CLC phase.<sup>[9]</sup> Similar observations were made for all derivatives (**n8-n14**) except **n7**. The compound **n7** melts to focal conic texture at 110.6 °C, which isotropizes at

114.9 °C. Absence of single wavelength reflection in *n*7 suggests the formation of a smectic phase. Dimesogenic compound *n*7 shows a cholesteric phase from 141.6 °C to 106.3 °C and a smectic phase from 106.3 °C to 58.5 °C in the cooling cycle. In the heating cycle SmA phase was observed only for small temperature range.

### 3.2. Thermal effects of cholesteric pitch

The molecular ordering of cholesteric liquid crystals in a helical arrangement induces reflection at the wavelength satisfying the equation  $\lambda_{\text{max}} = p/n$ , where  $\lambda_{\text{max}}$  is the reflection maximum,  $p$  is the pitch of the helix and  $n$  is the refractive index. Pitch length of a cholesteric LC can increase or decrease by temperature depending on the sign of the thermal coefficient  $\alpha$ , which is equal to  $1/p [dp/dT]$ , where  $p$  is the 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 with alkyl chain length 6 (*n*6) exhibit a reflection band at 494 nm at 140 °C, and the reflection band red shifted to 596 nm upon cooling to 100 °C. Maximum wavelength shift of 225 nm was observed in the case of *n*8. In this compound the  $\lambda_{\text{max}}$  shifted from 543 nm at 135 °C to 768 nm at 85 °C (Figure 1). Figure 2 shows the plot of reflected wavelength against the temperature of dimesogens.

Strong odd-even effects were observed as a function of spacer length and the selective reflection wavelength associated with the cholesteric liquid crystalline phase. The reflection band containing alkyl chain length with

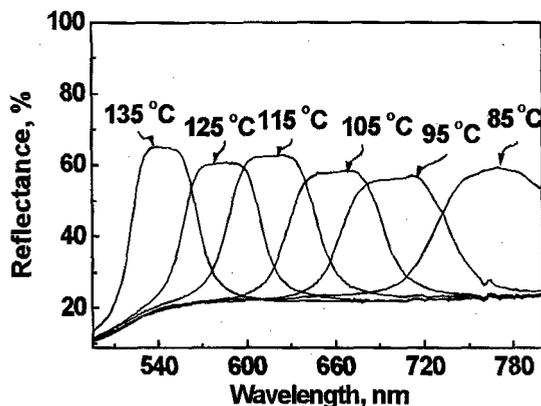


Fig.1 Dependence of selective reflection wavelength on the temperature of *n*8 in the cholesteric phase measured in the cooling cycle.

even number of carbon atoms shifts drastically compare to its odd counter parts (Figure 2). Also it has been found that in the compounds containing odd number of carbon atoms maximum reflection observed was  $< 450$  nm. Odd-even effect observed in the change in the reflection wavelength can be explained considering the molecular arrangements of the dimesogens.<sup>[10]</sup> In compounds having even number of methylene spacer units leads to a molecular shape, which allows the cholesteryl moiety to lie approximately parallel to the azobenzene. This conformation favors the formation of smectic clusters<sup>[10, 11]</sup> due to its rod shape. Compounds having odd number of carbon atoms in the spacer have slightly distorted rod shape. This structure destabilizes

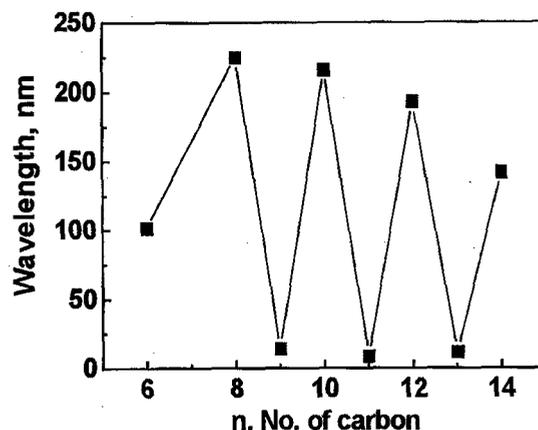


Fig.2. A plot of number of methylene spacers in the dimesogens against the thermal shift in reflected wavelength

the formation of smectic cybotactic groups even at low temperatures. This is further confirmed from x-ray diffraction studies.

### 3.3. Photoeffects of cholesteric pitch

Isomerization studies were carried out at stable cholesteric super cooled temperature using a high-pressure mercury lamp (500 W, Ushio) with 366 nm filter. Thin layers of the dimesogens were sandwiched between cover slips containing 10  $\mu\text{m}$  glass spacers and the film was heated to the isotropic state and slowly cooled to the desired cholesteric temperature. All measurements were performed within the temperature range where the cholesteric mesophase was stable. Photo irradiation of these films using 366 nm light leads to decrease in absorbance at 321 nm ( $\pi$ - $\pi^*$ ) regions and concomitant increase at 450 nm ( $n$ - $\pi^*$ ) regions. These changes can be attributed to the *trans* to *cis* photoisomerization of the azobenzene moiety present in the dimesogens, which is accompanied by a shift in the reflection band. Upon continuous photo irradiation, cholesteric to isotropic phase transition was observed because conversion from *trans* to the *cis* isomer leads to destabilization of the cholesteric phase due to its bent structure. Formation of small amount of *cis* isomer hypsochromically shifts the reflected wavelength. For

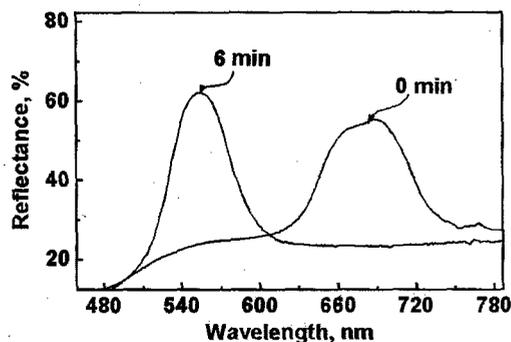


Fig.3 Reflection spectra of *n*-8 at 100 °C (cooling cycle) using 366 nm wavelength at different time intervals

example, in the dimesogen with alkyl chain length 8 (**n8**), photo irradiation using 366 nm shifted the maximum reflected wavelength from 684 to 553 nm (at 100 °C, cooling cycle, Fig. 3). Maximum shift in the reflection wavelength from 703 nm to 488 nm ( $\Delta\lambda = 215$  nm) was observed for **n12**. Microscopic molecular disordering caused by photoisomerization of the dimesogens gives analogous impact to the system with thermally induced disordering in the molecular arrangement.

### 3.4. Photochemical Phase Transitions of Liquid Crystalline states

Phase transition can be triggered by photochemical reactions of guest molecules doped in the liquid crystal matrices. There have been several reports on such photoinduced phase transitions of liquid crystals containing guest molecules such as azobenzene and spiropyran derivatives.<sup>[12]</sup> In liquid crystal containing azobenzene derivatives, the rod like shape of the *trans* form of the azobenzenes tend to stabilize the LC phase while the *cis* form tend to destabilize it. Thus, *trans-cis* photoisomerization of the azobenzene derivatives can lead to lowering of the LC to isotropic (I) phase transition temperature of the mixture. Photochemical phases transition from nematic to isotropic and smectic to isotropic have been reported. Other well-studied LC systems are nematic LC doped with photoactive chiral chromophores. Reversible photoswitching of LC phase between nematic and cholesteric in doped systems using circularly polarized light have also been described.

A smectic to cholesteric photoinduced phase change was observed in the case of dimesogen **7n7** (Fig 3).<sup>[6]</sup> Thin layers of the dimesogen **7n7** was sandwiched between cover slips containing 10  $\mu\text{m}$  glass spacers and the film was heated to the isotropic state and slowly cooled to 100 °C. At this temperature the film showed the focal conic fan shaped texture characteristic of smectic A phase. The film turned cholesteric on irradiation with light from a 500 W medium pressure mercury lamp, for 30 seconds filtered through a 366 nm filter, which was confirmed from the presence of selective violet reflection and the cholesteric texture. Photo irradiation of *trans-7n7* would lead to partial isomerization to its *cis* form. Cholesteric to isotropic phase transition was

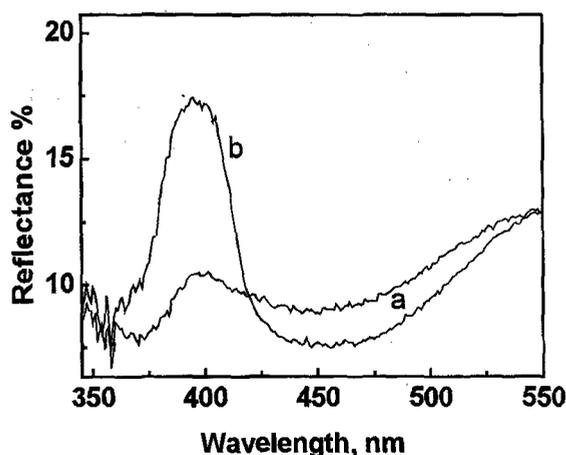


Fig.3 Reflection spectra of **7n7** at 100 °C (cooling cycle). a) before irradiation b) irradiated for 30 seconds using 366 nm wavelength.

observed upon continuous photo irradiation of the thin film of **7n7**, because conversion from *trans* to the *cis* isomer leads to the destabilization of the LC phase due to its bent structure. On keeping the irradiated isotropic film of **7n7** at same temperature (100 °C) *cis* to *trans* reversal of the dimesogen **7n7** was occurred, which change the phase to cholesteric and further to smectic A. Figure 3 show the reflection spectra obtained for **7n7** at 100 °C before and after photo irradiation studies. After photo irradiation for 30 seconds, a reflection band of 394 nm was observed, which was red shifted to 415 nm suggesting partial thermal reversal of *cis 7n7* back to its *trans* form. On keeping the film at same temperature for 60 seconds after the irradiation, SmA phase was completely regenerated.

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