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# Synthesis and Photoswitching Properties of Some Cholesterol Based Liquid Crystals

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The synthesis and photoswitching properties of some azobenzene linked cholesterol derivatives (**3a-d** and **5a,b**) have been described. Thermal properties of these compounds were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) techniques. Compounds **3a** and **3b** exhibit a Smectic A phase, whereas **3d** and **5b** exhibit Smectic A, TGB and cholesteric phases. Compounds **3c** and **5a** show a cholesteric mesophase. The presence of azobenzene moiety imparts photochromic properties to these compounds. *Trans-cis* photoisomerization of the azo-moiety in these compounds in eutectic mixtures consisting of cholesteryl oleyl carbonate, cholesteryl chloride and cholesteryl nonanoate was studied by irradiating at 355 nm. Irradiation of the thin films of these mixtures lead to *trans-cis* isomerization of the azobenzene chromophore present in the mixture which is accompanied by a large shift in the reflectance band resulting in visual changes in the colour of these films.

**Keywords:** Cholesterol linked mesogens; *cis-trans* isomerization; photoinduced pitch change

## INTRODUCTION

Liquid crystals can be switched by relatively modest electric and magnetic fields and are hence particularly suited for applications in nonlinear optics<sup>1-3</sup> and optical switching<sup>4</sup> devices. The molecular ordering of cholesteric liquid crystals in a helical arrangement induces reflection at the wavelength satisfying the relationship  $\lambda = np$ , where  $n$  is the refractive index of the liquid crystalline material and  $p$  is the helical pitch.<sup>5</sup> The pitch of the helix of cholesteric liquid crystal is sensi-

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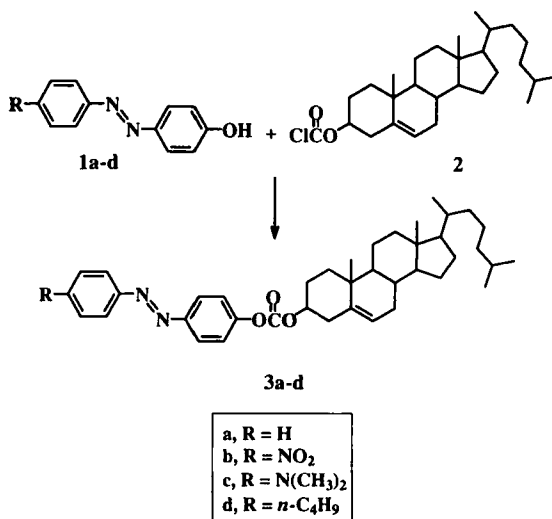
tive to the presence of dissolved molecules<sup>6</sup> and photochemical transformations of such guest molecules are known to induce optical changes in cholesteric liquid crystals.<sup>7–11</sup> Recent studies on the photoswitching of nematic and smectic liquid crystals have however shown that liquid crystalline materials that are inherently photoactive have much faster switching times.<sup>12–15</sup>

In this report, the synthesis as well as photoswitching properties of some azobenzene linked cholesterol derivatives are described. The azobenzene moiety can impart both nonlinear optical as well as photoswitching properties to the liquid crystalline materials. These properties in conjunction with the electrooptic switching properties of liquid crystals can lead to interesting materials for nonlinear optical and photoswitching applications. Photoinduced ionic conductivity and photogelation properties of some azobenzene linked cholesterol derivatives have been reported earlier.<sup>16–18</sup>

## RESULTS AND DISCUSSION

### Synthesis

Cholesterol derivatives were synthesized by refluxing cholesteryl chloroformate and the corresponding azo compound in benzene as per Schemes 1 and 2. All compounds were characterised on the basis of spectral and analytical data.<sup>19</sup>

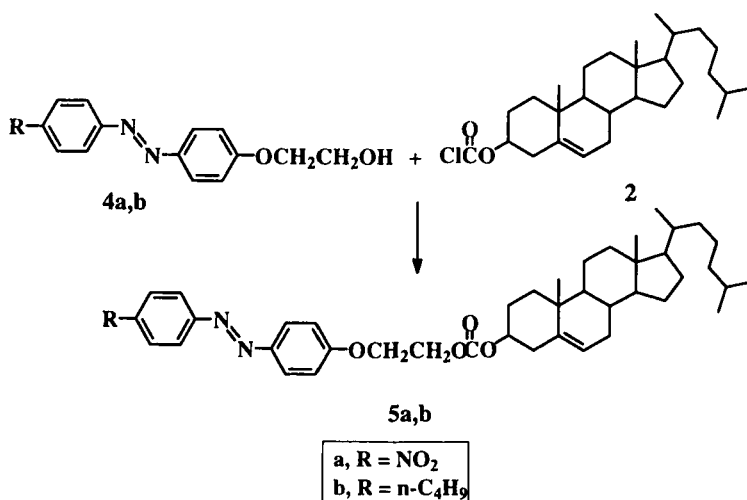


SCHEME 1

## Thermal Studies

Phase transition characteristics of these compounds were studied by differential scanning calorimetry (DSC), hot stage polarized optical microscopy (POM) and X-ray diffraction. POM of **3a** showed a focal conic texture characteristic of a Smectic A phase<sup>20</sup> on first heating and cooling (Figure 1a). The phase transition temperatures were reproducible over several heating and cooling cycles. DSC measurements showed only the transition from crystalline to smectic phase on heating and a crystallization exotherm on cooling. No isotropization endotherm was observed in DSC. The same transition pattern was observed for **3b**. Compounds **3c** and **5a** showed oily streak textures in the heating cycle and focal conic textures in the cooling cycle, which are characteristic of cholesteric phases.<sup>20</sup>

Compounds **3d** and **5b** showed a boundry phase (TGB) (Figure 1b), along with smectic and cholesteric phases. The assignment of TGB phase was made from the observation of the characteristic vermis texture.<sup>21</sup> The structures of the mesophases of compounds **3d** and **5b** were also examined by X-ray diffraction which confirms the smectic A phase of these compounds below 180 °C. Diffraction pattern of **3d** at 145 °C shows one sharp ring at 34.9 Å and a diffused outer ring at 5.2 Å. Spacings were same at 170 °C and 180 °C. Compound **5b** also showed the similar diffraction pattern at 145 °C, 170 °C and 180 °C.



SCHEME 2

Apart from **3a**, these compounds did not show reproducible phase changes upon repeated heating and cooling cycles which could be attributed to their ther-

mal instability. The decomposition temperatures of these compounds other than **3a** are close to or below their isotropization temperature (Table I).

TABLE I Phase transition properties of **3a-d** and **5a, b** examined by DSC and POM techniques

| Compound  | Decomposition temp. (TGA) | DSC <sup>a</sup> $T_h$ (°C) | POM <sup>b</sup> (°C)                                    |
|-----------|---------------------------|-----------------------------|--|
| <b>3a</b> | 270                       | 172, 240                    | K170 S <sub>A</sub> 221 I<br>I 220 S <sub>A</sub> 120 K  |
| <b>3b</b> | 273                       | 208, 265                    | K 202 S <sub>A</sub> 266 I<br>I 242 S <sub>A</sub> 186 K |
| <b>3c</b> | 110                       | 205                         | K 196 Ch 231 I   |
| <b>3d</b> | 271                       | 138                         | K138 S <sub>A</sub> 194 TGB 195.3 Ch 254 I               |
| <b>5a</b> | 268                       | 220                         | K 216 Ch 264 I<br>I 233 Ch 174 K                         |
| <b>5b</b> | 271                       | 135                         | K 135 S <sub>A</sub> 187.6 TGB 189 Ch 252 I              |

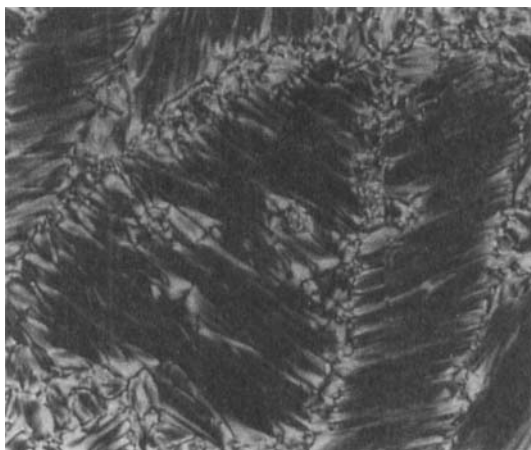
a. First heating cycle;  $T_h$  = transition temperatures on heating;

b. K = crystalline; S<sub>A</sub> = smectic A; Ch = cholesteric; TGB = Twisted grained boundry phase; I = isotropic phase.

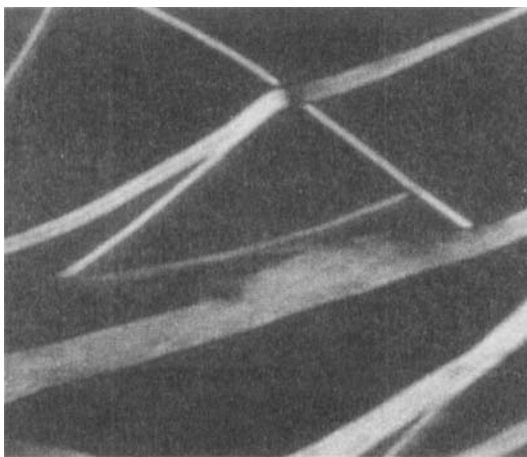
### Photoinduced Pitch Change of Liquid Crystalline Films

Thin films consisting of the cholesterol derivatives were prepared by dissolving 10 mol percentage of compounds **3a-d** and **5a,b** in a cholesteric mixture consisting of cholesteryl oleyl carbonate (COC), cholesteryl chloride (CC) and cholesteryl nonanoate (CN) in the ratio 11:26:42 respectively, in each case, by weight. The eutectic mixture showed cholesteric phase up to 71 °C. Thin layers of mixtures were sandwiched between glass plates previously rubbed unidirectionally with 0.25 µm of diamond paste. Mylar spacers of 0.03 mm thickness were placed between these plates. Transparent films with planar textures were obtained when the eutectic mixtures were sheared between the glass plates, in each case. These mixtures were adjusted so as to show selective reflection in the visible region of the spectrum. All measurements were performed within the temperature range where the cholesteric mesophase was stable.

Irradiation of these films by 355 nm leads to a decrease in absorbance in the 355 nm region and increase in absorbance in the 450 nm region. These changes can be attributed to the *trans* to *cis* isomerization of the azobenzene moiety (Scheme 3) brought about by UV irradiation. The isomerization of the azo-moiety is accompanied by a large shift in the reflectance band, indicating an increase in the pitch of the liquid crystalline mixture. The changes obtained on irradiation of a mixture of COC, CC and CN containing 10 mol percent of **5b**, are shown in



(a)

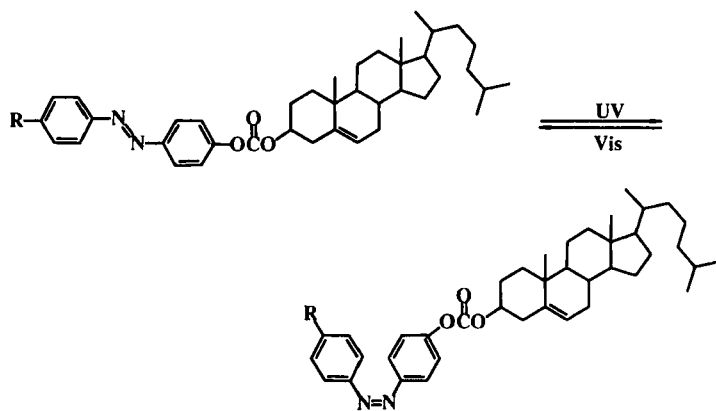


(b)

FIGURE 1 (a) Focal conic texture of smectic phase of **3a**. (b) TGB phase of **3d** (See Color Plate VIII at the back of this issue)

Figure 2. Figure 3 shows the shift of reflectance band as a function of irradiation time for the eutectic mixture of **3a**. Similar results were obtained for eutectic mixtures containing **3d** and **3c**. In all these studies the change in reflectance band

( $\Delta\lambda$ ) reaches maximum within about 100–200 seconds of irradiation. Table II shows the maximum shift in  $\lambda_{\max}$  of reflectance band on irradiation for these mixtures. The maximum change in reflectance band from 590 nm to 700 nm ( $\Delta\lambda = 110$  nm) was observed for the eutectic mixture containing **5b**. This change could also be perceived visually as the colour change of the irradiated portion of the film from green to red. Compounds **3b**, **3c** and **5a** showed the least change in reflectance band. This may be attributed to the ability of donor-acceptor substituted azobenzene moieties to undergo rapid *cis-trans* isomerization.<sup>22</sup> Hence, in molecules containing nitro and amino groups the steady state concentration of the *cis* form could be expected to be very low resulting in a smaller shift in the reflectance band.



SCHEME 3

TABLE II Maximum change of reflectance band of eutectic mixtures of **3a-d** and **5a,b** upon irradiation for 5 min at 60 °C

| Compound  | $\Delta\lambda$ nm |
|-----------|--------------------|
| <b>3a</b> | 53                 |
| <b>3b</b> | 5                  |
| <b>3c</b> | 23                 |
| <b>3d</b> | 59                 |
| <b>5a</b> | 4                  |
| <b>5b</b> | 110                |

The switching time of the thin film was measured by laser flash photolysis. The thermostated film was irradiated using the third harmonic of a Nd:YAG laser



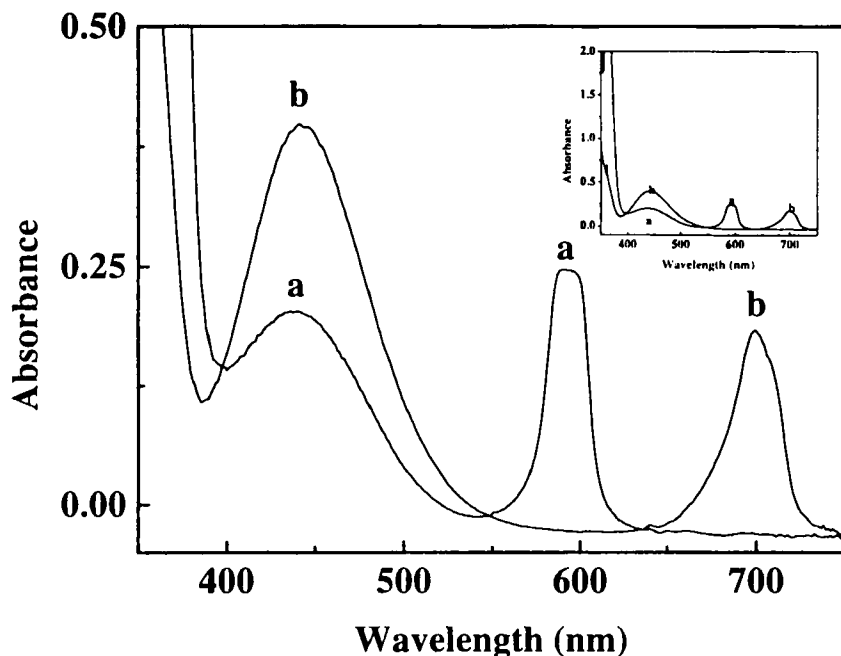


FIGURE 2 Absorption spectra of eutectic mixture of 5b; (a) before irradiation and (b) after irradiation

pulse (10 ns). The change in transmittance of the probe light at 600 nm isolated using a monochromator was measured using a photomultiplier and recorded on a 500 MHz Philips oscilloscope (545208). Figure 4 shows the time resolved measurement of the photochemical colour switching of the thin film of **5b** by pulsed irradiation at room temperature. Upon irradiation, the transmittance at 600 nm increases and reached a stable value within 40 ms. The *trans-cis* photoisomerization occurs within the laser pulse. The switching time however will be defined by the time required for the liquid crystalline mixture to reorient to the new pitch. Visual colour change of the film from green to red could be obtained with single pulse from the laser.

The thermal *cis-trans* isomerization, which occurs over very long periods depending on the temperature of the film, is accompanied by a return of the reflectance band to its original value. These effects are shown in Figure 5 for the eutectic mixture of compounds **5b**.

The *cis-trans* isomerization, that occurs in the dark follows first order kinetics and the rate constant for these processes calculated using the rate equation of the

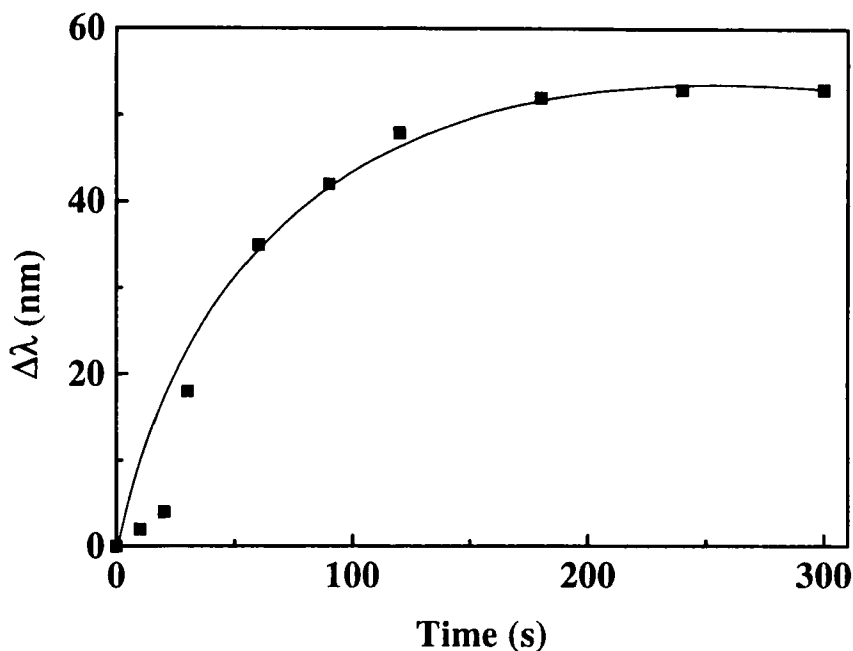


FIGURE 3 Change of reflectance band ( $\Delta\lambda$ ) of eutectic mixture of **3a** on irradiation time at 60 °C

first order kinetics for **3a** are shown in Table III. From the plot of  $\log k$  versus temperature, the activation energy of the process calculated using the Arrhenius equation was  $92.71 \text{ kJmol}^{-1}$ . The reported activation energy of photoisomerization of azobenzene in *n*-heptane is  $94.05 \text{ kJmol}^{-1}$ .<sup>23</sup> This shows that even though the bulk viscosity of the liquid crystal matrix is greater than that of *n*-heptane, the microviscosity around the azo moiety is the same in both these cases.

TABLE III Rate of *cis-trans* isomerization of a eutectic mixture of **3a** at different temperatures

| $T (K)$ | $k (sec^{-1})$        |
|---------|-----------------------|
| 316     | $4.10 \times 10^{-3}$ |
| 323     | $4.50 \times 10^{-3}$ |
| 333     | $1.50 \times 10^{-2}$ |
| 343     | $2.83 \times 10^{-2}$ |
| 353     | $1.75 \times 10^{-1}$ |

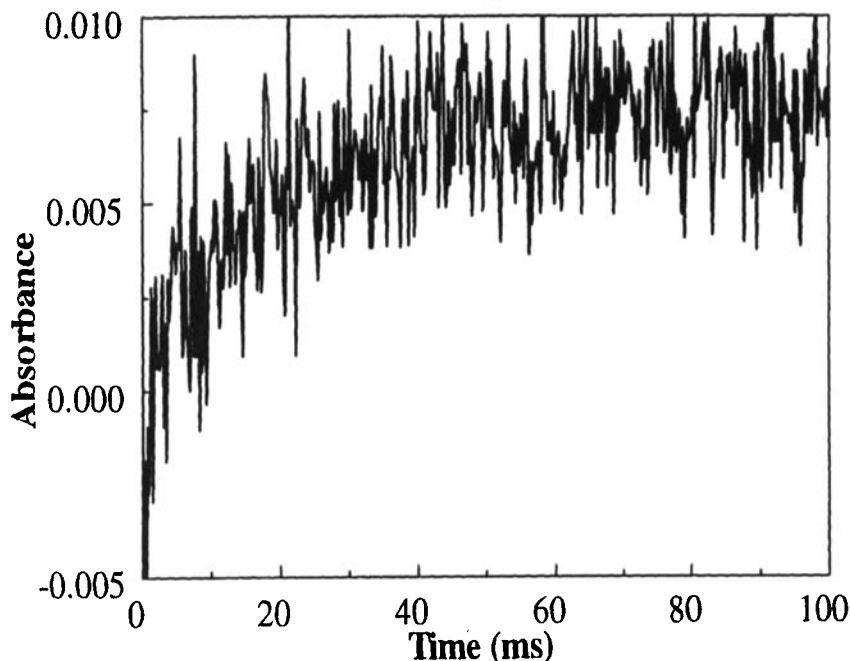


FIGURE 4 Growth of reflectance band at 600 nm measured by pulsed irradiation of eutectic mixture of 5b at 355 nm

Most photochromic molecules can change their molecular shape upon photoirradiation, and this property has been used extensively to control the orientation of LCs by light.<sup>12–15</sup> For instance, the *trans*-form of azobenzene derivatives is rod-like, which stabilizes the LC phase, whereas the *cis* form is bent and destabilizes the LC phase. Therefore the *trans-cis* photoisomerization of azobenzenes in LC phase can cause disorganization of the phase structure. This leads to a change in the pitch length and consequently, a change in the reflectance wavelength.

## CONCLUSIONS

Azobenzene linked cholesterol derivatives showing liquid crystalline characteristics have been synthesized and characterized. Photoirradiation of eutectic mixtures of these materials with cholesteric liquid crystals brought about visual changes in the colour of the film indicating that these materials can be used in optically active display devices.

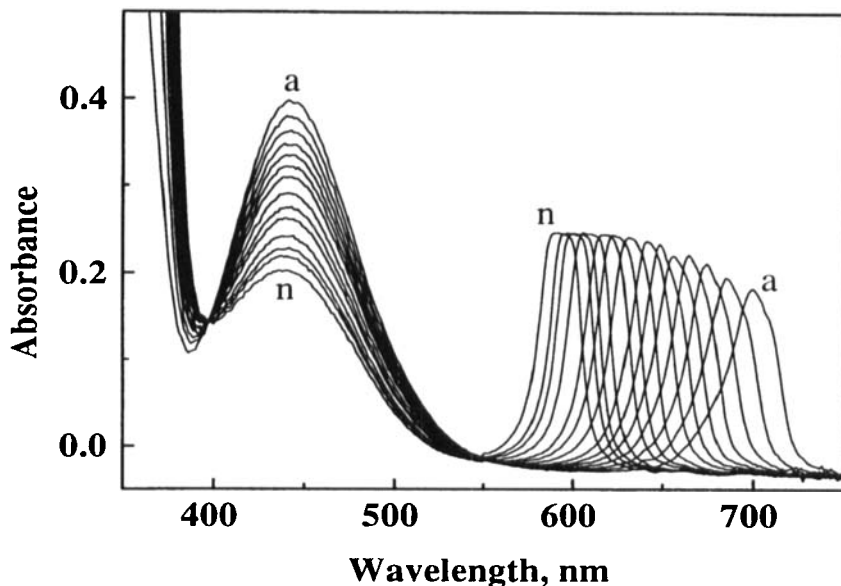


FIGURE 5 Change of cholesteric pitch of eutectic mixture of 5b, at different time intervals after irradiation at 60 °C for 5 min. a) 0 min, b) 5 min, c) 10 min, d) 15 min, e) 20 min, f) 25 min, g) 30 min, h) 40 min, i) 50 min, j) 60 min, k) 80 min, l) 100 min, m) 120 min, n) 200 min

## EXPERIMENTAL SECTION

Phase transitions were observed under Nikon HFX 35A Optiphot polarized light microscope equipped with Linkam THMS 600 heating and freezing stage connected to Linkam TP92 temperature programmer. DSC scans were performed using Du Pont DSC 2010 Differential Scanning Calorimeter attached to Thermal Analyst 2100 data station under air (heating rate was 5 °C/min in all cases). X-ray diffraction studies has been carried out using Cu K $\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ) radiation obtained from rotating X-ray generator (Rigaku) and the diffraction pattern was collected on a image plate detector (Marresearch).

Steady state photolyses were carried out on an ORIEL optical bench using a 200 W high pressure mercury lamp. Monochromatic light (intensity =  $9.3 \times 10^{-8}$  Einsteins/min) was obtained by using a 350 nm band pass filter. Eutectic mixtures of the cholesterol derivatives **3a-d** and **5a,b** were prepared by melting 10 mol percentage of the corresponding compound in cholesteric mixture consisting of cholesteryl oleyl carbonate (COC), cholesteryl chloride (CC) and cholesteryl nonanoate (CN) in the ratio 55:130:210, respectively, by weight. The

temperature of the film was kept constant by circulating water of the desired temperature through the film holder. The reflection and absorption studies were carried out either on Shimadzu UV 2100 or GBC UV spectrophotometers.

## MATERIALS

Reagent grade reactants and solvents were used as received from chemical suppliers. Extremely dry solvents were prepared as per standard procedures. Spectroscopic grade solvents were used for all measurements. Cholesteryl oleyl carbonate and cholesteryl nonanoate were purchased from Aldrich Chemical Co. USA and used without further purification. Cholesteryl chloride purchased from Aldrich Chemical Co. USA was further purified by column chromatography, using hexane as eluent. Azobenzene derivatives were prepared by adopting standard procedures.<sup>19,24</sup>

## Acknowledgements

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## Supplementary Material

### GENERAL PROCEDURE FOR THE SYNTHESIS OF CHOLESTERYL DERIVATIVE OF AZOBENZENES

Equimolar amounts of azobenzene derivative and pyridine were dissolved in benzene and to it was added a solution of an equivalent amount of cholesteryl chloroformate in benzene. The contents were refluxed for 1 h, the precipitated salt was removed by filtration and the benzene solution of the product was purified by column chromatography over silica gel (100–200 mesh). Elution with toluene gave the pure products as reddish yellow solids. The products were further purified by recrystallization from a mixture (1:1) of toluene and petroleum ether (bp 60–80 °C).

#### Cholesteryl azophenyl carbonate (3a)

This compound was prepared from cholesteryl chloroformate (2.28 g, 5.07 mmol) and 4-hydroxyazobenzene (1 g, 5.07 mmol). The product was purified by column chromatography to give 2.81 g (91%) of the title compound, which melted at 221 °C, after recrystallization from a mixture (1:1) of toluene and petroleum ether. IR  $\nu_{\text{max}}$  (KBr): 2942, 2900, 2876 (CH), 1768 (C=O), 1590 (C=C)  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ): 333 nm ( $\epsilon$  17950  $\text{M}^{-1}\text{cm}^{-1}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.63–0.65 (3 H, s, cholesteric), 0.66–2.05 (38 H, m, cholesteric), 2.49–2.52 (2 H, d, cholesteric), 4.4–4.6 (1 H, m, OCH), 5.3–5.6 (1 H, m, vinylic) 6.70–6.90 (3 H, m, aromatic), 7.20–7.50 (2 H, d, aromatic) 7.80–8.10 (4 H, d, aromatic);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.81, 18.67, 19.18, 21.00, 22.52, 22.76, 23.83, 24.22, 27.65, 27.92, 28.16, 31.80, 35.74, 36.16, 36.48, 36.78, 37.89, 39.47, 39.68, 40.15, 42.24, 49.94, 56.15, 56.59, 78.79, 111.40, 121.31, 123.16, 124.95, 139.06, 139.36, 143.56, 150.75, 151.74, 152.36, 152.57. Exact mol wt calcd for  $\text{C}_{40}\text{H}_{55}\text{N}_2\text{O}_3$  ( $\text{MH}^+$ ) 611.4213; found 611.4196 (FAB, high resolution mass spectroscopy).

#### Cholesteryl 4-nitroazophenyl carbonate (3b)

Treatment of cholesteryl chloroformate (560 mg, 1.25 mmol) and 4-nitro-4'-hydroxyazobenzene (305 mg, 1.25 mmol) gave a crude product, which was further purified by chromatography. Recrystallization from a mixture (1:1) of toluene and petroleum ether gave 458 mg (56%) of a pure sample of **3b**, mp

266°C. IR  $\nu_{\max}$  (KBr): 2957, 2897, 2871 (CH), 1751 (C=O), 1594 (C=C)  $\text{cm}^{-1}$ ; UV  $\lambda_{\max}$  ( $\text{CHCl}_3$ ): 343 nm ( $\epsilon$  11480  $\text{M}^{-1}\text{cm}^{-1}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.67–0.69 (3 H, s, cholesteric), 0.85–2.04 (38 H, m, cholesteric), 2.49–2.52 (2 H, d, cholesteric), 4.2–4.7 (1 H, m, OCH), 5.3–5.6 (1 H, m, vinylic), 7.30–7.50 (2 H, d, aromatic), 7.90–8.20 (4 H, m, aromatic), 8.30–8.50 (2 H, m, aromatic);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.81, 18.67, 19.21, 21.00, 22.52, 22.76, 23.83, 24.22, 27.62, 27.95, 28.16, 31.83, 35.74, 36.16, 36.51, 36.81, 37.89, 39.50, 39.68, 42.27, 49.97, 56.15, 56.65, 79.27, 121.81, 122.77, 123.30, 123.39, 124.68, 128.26, 138.97, 139.42, 148.75, 149.86, 152.27, 154.06, 155.53. Exact mol wt calcd for  $\text{C}_{40}\text{H}_{54}\text{N}_3\text{O}_5$  ( $\text{MH}^+$ ) 656.4063; found 656.4051 (FAB, high resolution mass spectroscopy).

### Cholesteryl 4-N,N-dimethylaminoazophenyl carbonate (3c)

Compound **1c** was synthesized from cholesteryl chloroformate (500 mg, 1.2 mmol) and 4-N,N-dimethylamino-4'-hydroxyazobenzene (270 mg, 1.12 mmol). The product was recrystallized from a mixture (1:1) of toluene and petroleum ether to afford 620 mg (85%) of the title compound, mp 231 °C.

IR  $\nu_{\max}$  (KBr): 2952, 2872 (CH), 1766 (C=O), 1524 (C=C)  $\text{cm}^{-1}$ ; UV  $\lambda_{\max}$  ( $\text{CHCl}_3$ ): 413 nm ( $\epsilon$  16350  $\text{M}^{-1}\text{cm}^{-1}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.66–0.84 (3 H, s, cholesteric), 0.88–2.05 (38 H, m, cholesteric), 2.48–2.51 (2 H, d, cholesteric), 3.10 (6 H, s,  $\text{N}(\text{CH}_3)_2$ ), 4.3–4.7 (1 H, m, OCH), 5.3–5.6 (1 H, m, vinylic), 7.30–7.70 (4 H, m, aromatic), 7.80–8.20 (4 H, m, aromatic);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.81, 18.70, 19.21, 21.00, 22.55, 22.79, 23.83, 24.22, 27.59, 27.95, 28.16, 31.80, 35.74, 36.19, 36.48, 36.78, 37.89, 39.50, 39.68, 42.27, 49.94, 56.15, 56.62, 79.00, 121.54, 122.86, 123.19, 123.99, 128.97, 130.97, 139.00, 150.16, 152.42, 152.51, 153.02. Exact mol wt calcd for  $\text{C}_{42}\text{H}_{55}\text{N}_2\text{O}_3$  ( $\text{MH}^+$ ) 654.4635; found 654.4603 (FAB, high resolution mass spectroscopy).

### Cholesteryl 4-butylazophenylcarbonate (3d)

Treatment of cholesteryl chloroformate (3 g, 6.68 mmol) with azobenzene derivative **1d** (1.75 g, 6.68 mmol) gave the crude product which was further purified by column chromatography. Recrystallization from a mixture (1:1) of toluene and petroleum ether gave 4.2 g (94%) of the title compound, which melted at 254°C. IR  $\nu_{\max}$  (KBr): 3070, 2927, 2884 (CH), 1711 (C=O), 1607, 1598 (C=C)  $\text{cm}^{-1}$ ; UV  $\lambda_{\max}$  ( $\text{CHCl}_3$ ): 338 nm ( $\epsilon$  22250  $\text{M}^{-1}\text{cm}^{-1}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.64 (3 H, s, cholesteric), 0.65–2.05 (45 H, m, cholesteric and butyl), 2.52–2.65 (2 H, d, cholesteric), 2.69–2.72 (2 H, t,  $\text{CH}_2$ ), 4.4–4.6 (1 H, m, OCH), 5.4 (1 H,



m, vinylic), 7.1–7.4 (4 H, m, aromatic), 7.8–8.1 (4 H, m, aromatic),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.78, 13.87, 18.67, 19.18, 20.97, 22.28, 22.52, 22.76, 23.86, 27.56, 27.92, 31.77, 33.29, 35.53, 35.74, 36.16, 36.45, 36.78, 37.89, 39.47, 42.21, 49.88, 56.12, 56.56, 78.91, 121.45, 122.86, 123.16, 123.84, 128.94, 138.97, 146.43, 150.22, 150.75, 152.39, 152.75. Exact mol wt calcd for  $\text{C}_{44}\text{H}_{63}\text{N}_2\text{O}_3$  ( $\text{MH}$ ) $^+$  667.4839; found 667.4849 (FAB, high resolution mass spectroscopy).

### Cholesteryl 4-nitro-4'-ethoxyazophenyl carbonate (5a)

Compound **5a** was prepared from cholesteryl chloroformate (1.65 g, 3.66 mmol) and 4-nitro-4'-ethoxyazobenzene (1 g, 3.66 mmol). The product was purified by column chromatography to give 2.42 g (96%) of the title compound, which melted at 264 °C, after recrystallization from a mixture (1:1) of toluene and petroleum ether. IR  $\nu_{\text{max}}$  (KBr): 2950, 2873 (CH), 1770 (C=O), 1613 (C=C)  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ): 340 nm ( $\epsilon$  28350  $\text{M}^{-1}\text{cm}^{-1}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.67–0.69 (3 H, s, cholesteric), 0.84–2.11 (40 H, m, cholesteric), 2.41–2.49 (2 H, d, cholesteric), 2.49–2.52 (2 H, t,  $\text{OCH}_2$ ), 4.35–4.70 (1 H, m, OCH), 5.2–5.6 (1 H, vinylic), 7.2–7.6 (2 H, d, aromatic), 7.8–8.1 (4 H, d, aromatic), 8.2–8.5 (2 H, d, aromatic);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.84, 18.70, 19.24, 21.06, 22.55, 22.79, 23.83, 24.25, 27.62, 27.98, 28.19, 31.86, 35.77, 36.19, 36.54, 36.84, 37.89, 39.50, 39.71, 42.30, 50.00, 56.18, 56.68, 79.30, 121.84, 123.42, 124.68, 139.00, 148.78, 149.89, 152.27, 154.09, 155.56. Analysis calcd for  $\text{C}_{42}\text{H}_{57}\text{N}_3\text{O}_6$ : C, 72.07, H, 8.21, N, 6.00; found C, 72.51, H, 8.19, N, 6.14.

### Cholesteryl 4-butylazo (4-ethoxyphenyl)carbonate (5b)

Treatment of cholesteryl chloroformate (3 g, 6.68 mmol) with the azobenzene derivative **4b** (2 g, 6.68 mmol) gave a crude product which was further purified by column chromatography. Recrystallization from a mixture (1:1) of toluene and petroleum ether gave 4.15 g (87%) of a pure sample of **5b**, which melted at 250 °C. IR  $\nu_{\text{max}}$  (KBr): 2938, 2868 (C-H), 1768 (C=O), 1588, 1544  $\text{cm}^{-1}$ ; UV  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ): 335 nm ( $\epsilon$  21470  $\text{M}^{-1}\text{cm}^{-1}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.64 (3 H, s, cholesteric), 0.68–2.05 (47 H, m, aliphatic), 2.49–2.52 (2 H, d, cholesteric), 2.65–2.72 (2 H, t,  $\text{OCH}_2$ ), 4.4–4.7 (1 H, m, OCH), 5.3–5.5 (1 H, m, vinylic), 7.1–7.4 (4 H, m, aromatic), 7.7–8.1 (4 H, m, aromatic);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  11.57, 13.69, 18.49, 18.97, 20.82, 22.10, 22.34, 22.58, 23.69, 24.01, 27.38, 27.74, 27.98, 31.59, 33.11, 35.32, 35.56, 35.98, 36.25, 36.57, 37.68, 39.29, 42.03, 49.70, 55.94, 56.35, 78.80, 121.25, 122.68, 122.95, 123.63, 128.73, 138.76, 146.22, 150.01, 150.54, 152.18, 152.57. Analysis calcd for  $\text{C}_{46}\text{H}_{66}\text{N}_2\text{O}_4$ : C, 77.69, H, 9.35, N, 3.94; found C, 79.13, H, 9.22, N, 4.57.