

# Photochemical Phase Transition and Molecular Realignment of Glass-Forming Liquid Crystals Containing Cholesterol/Azobenzene Dimesogenic Compounds

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We synthesized dimesogenic liquid crystals with both cholesterol and azobenzene groups by esterification of 10,12-docosadiynoic acid or docosanedioic acid with 4-alkyl-4'-hydroxyazobenzene (or 4-hydroxyazobenzene) and cholesterol and studied the thermal, optical, and glass-forming properties. Especially, we focused on the effect of the length of the alkyl chain substituted on the azobenzene unit and the photochemical isomerization of the azobenzene unit on the properties of the mesophases of the compounds or a host cholesteric liquid crystal forming stable glass when using them as a dopant. Two compounds without an alkyl chain on the azobenzene unit show a cholesteric phase, while five compounds with an alkyl chain from butyl to hexadecyl show only a smectic phase. The cholesteric reflection bands of the compounds without an alkyl chain on the azobenzene unit shifted toward shorter wavelengths upon photoisomerization of the azobenzene unit from the trans to cis form. Further photoirradiation induced an isotropic phase in the compounds. The compounds with an alkyl chain showing a smectic phase directly changed to an isotropic phase after the photochemical formation of a certain amount of the cis form. All compounds attained a glassy state by maintaining a molecular order if the compounds between the substrates were rapidly cooled from their liquid-crystalline temperature to 0 °C. When the compounds were doped with 2–10 wt % of a dicholesteryl ester forming a stable cholesteric glass, the cholesteric band of the mixtures shifted toward shorter wavelengths following the photoisomerization from trans to cis of the azobenzene unit on the dopant. The extent of the shift depends on the irradiation energy, temperature, and length of the alkyl chain on the azobenzene unit. The mixture went into the glassy state, keeping the shifted cholesteric reflection band after rapid cooling from the liquid-crystalline temperature to 0 °C. The cholesteric glassy state was stable up to 80 °C. Since the molecular arrangement of the liquid-crystalline compounds and the conformation of the azobenzene unit completely returned to the initial state upon reheating to its isotropic temperature, the photoresponsibility and glass-forming property of the compounds or mixtures are applicable to rewritable recording materials.

## Introduction

There are many studies on the effect of the photochemical reaction of doped photochromic compounds on the molecular order of the host liquid crystals.<sup>1,2</sup> The reversible structural change induced by photoirradiation of photochromic compounds such as azobenzene,<sup>3–11</sup>

azoxybenzene,<sup>4</sup> stilbene,<sup>3,4</sup> spiroopyran,<sup>12</sup> thioindigo,<sup>13,14</sup> fulgide,<sup>15</sup> thienyl ethene,<sup>16</sup> arylidene-*p*-menthane-3-one,<sup>17</sup> and chiral thioxantene-based alkene<sup>18</sup> changes the intermolecular interaction between the guests and

(9) Sung, J.-H.; Hirano, S.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *Chem. Mater.* **2000**, *14*, 385.

(10) Ruslim, C.; Ichimura, K. *J. Phys. Chem. B* **2000**, *104*, 6529.

(11) Legge, C. H.; Mitchell, G. R. *J. Phys. D: Appl. Phys.* **1992**, *25*, 492.

(12) Kurihara, S.; Ikeda, T.; Tazuke, S.; Seto, J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3251.

(13) Dinescu, L.; Lemieux, R. P. *Liq. Cryst.* **1996**, *20*, 741.

(14) Dinescu, L.; Lemieux, R. P. *J. Am. Chem. Soc.* **1997**, *119*, 8111.

(15) Yokoyama, Y.; Sagisaka, T. *Chem. Lett.* **1997**, 687.

(16) Yamaguchi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **2000**, *345*, 287.

(17) Yarmolenko, S. N.; Kutulya, L. A.; Vashchenko, V. V.; Chepeleva, L. V. *Liq. Cryst.* **1994**, *16*, 877.

(18) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *J. Am. Chem. Soc.* **1995**, *117*, 9929.

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† Present address: Oji Paper Co. Ltd.

‡ Present address: University of Tokyo.

(1) Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.

(2) Ikeda, T.; Kanazawa, A. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1715.

(3) Sackmann, E. *J. Am. Chem. Soc.* **1971**, *93*, 7088.

(4) Pelzl, G. *Z. Chem.* **1977**, *17*, 294.

(5) Leier, C.; Pelzl, G. *J. Prakt. Chem.* **1979**, *321*, 197.

(6) Ogura, K.; Hirabayashi, H.; Uejima, A.; Nakamura, K. *Jpn. J. Appl. Phys.* **1982**, *21*, 969.

(7) Tazuke, S.; Kurihara, S.; Ikeda, T. *Chem. Lett.* **1987**, 911.

(8) Lee, H.-K.; Doi, K.; Harada, H.; Tsutsumi, O.; Kanazawa, A.; Shiono, T.; Ikeda, T. *J. Phys. Chem. B* **2000**, *104*, 7023.

host liquid crystals and induces a change in the molecular alignment of liquid crystals or a phase transition in some case. If the photochromic compound shows a liquid-crystalline phase, its photochemical reaction induces a molecular order change in itself.<sup>19</sup> Since the optical property of compounds changes depending on the molecular order, the phenomenon of the photoresponsive liquid crystals can be applied to the optical recording working in a photon mode.

If we apply this phenomenon to rewritable recordings, the temporal stability of the changed molecular order after the photoreaction is important since it should make storage and safe read-out of the memory possible. This is one of the reasons why the study of a photoresponsive liquid-crystalline polymer attracts much attention,<sup>20–22</sup> although realignment of the polymeric liquid crystal upon photoreaction is generally slow due to its high molecular weight.<sup>23–29</sup>

Recently, we synthesized a nonpolymeric cholesteric liquid crystal forming a stable glass<sup>30–34</sup> and reported the results on the fixation in a glassy state of the photochemically controlled helical molecular order.<sup>35–37</sup> The reflection band due to the cholesteric molecular order of the dicholesteryl ester over 1000 mass units is shifted toward the longer wavelength by doping 1–2 wt % of achiral trans-azobenzenes substituted with appropriate alkyl chains on the 4- and 4'-positions. Upon photochemical isomerization of the azobenzene from trans to cis, the reflection band continuously shifted toward shorter wavelengths. By cooling after the irradiation, the liquid-crystalline state turned into a glassy state, and the shifted reflection band was fixed. Although this two-component system containing a dialkylazobenzene and glass-forming dicholesteryl ester realized full color rewritable recording in a photon mode, the thermal stability of the glassy state of the cholesteric dicholesteryl ester is decreased by the increase in the

content of the dialkylazobenzene. To solve the problem of destabilization of the glassy state of the mixture, we synthesized new alkylazobenzene derivatives having a cholesterol group. In this paper, we report the liquid-crystalline and photoresponsive properties of these compounds and also the property as a photoresponsive dopant in a glass-forming dicholesteryl ester.

## Experimental Section

**General Methods.** The NMR spectra of all intermediates and final compounds were recorded on a JEOL GX 270 spectrometer. The optical textures of the mesophases were observed using a polarizing microscope (Olympus BX60) equipped with a hot stage (Mettler, FP82 and FP90). The transmission and reflection spectra were recorded on UV–vis spectrophotometers (Hewlett-Packard 8453 and Otsuka Electronics MCPD-1000, respectively). DSC measurements were performed on 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 to a radiation beam for 15 s with a 150-mm camera length.

The mixtures of **1** and the azobenzenes **3a–e** (Scheme 1) were prepared by evaporation of dichloromethane from their mixed solutions. The cholesteric liquid-crystalline samples of the mixtures were prepared between two glass or quartz plates with temperature control using a hot stage (Mettler, FP82 and FP90). A high-pressure mercury lamp (Ushio, 500 W) with appropriate glass filters (for irradiation at 366 nm, Toshiba Glass Co., UV-35 + UVD-36C, and for 436 nm, Ealing Electro-Optics, Inc., #35-3334) was employed as the irradiation source. A 325-nm light emitted from a He–Cd laser (Kimmon, Model IK3102R-G, 100 mW) was employed for image recording. The laser was modulated and scanned with an ultrasonic modulator (IntraAction Corp., Model ASM-702B2) and an X–Y galvano mirror (General Scanning Inc., Model 2ST/MiniSAX) following the image data provided as a jpeg file from a personal computer.

**Materials.** Dicholesteryl-10,12-docosadiynoate **1** was synthesized by a previously reported method.<sup>30</sup>

The 4-alkyl-4'-hydroxyazobenzenes **2a–e** were synthesized by similar previously reported procedures.<sup>38</sup>

**2c.** *p*-*n*-dodecylaniline (3.42 g, 13.1 mmol) was dissolved in 1:1 aqueous acetone (33 mL) solution, and concentrated HCl (3.3 mL) was then added. The mixture was cooled in an ice bath, and sodium nitrate (0.93 g) dissolved in 17 mL of cold water was added with stirring. After addition, the solution was allowed to stand for 15 min in an ice bath. The obtained diazonium salt solution was slowly added to a cold aqueous solution (33 mL) of phenol (1.3 g), sodium hydroxide (0.57 g), and sodium carbonate (2.3 g). After 15 min of stirring, a dark brown precipitate appeared, which was filtered out and recrystallized from a mixed solvent of benzene and hexane. A total of 3.56 g of an orange product was obtained. Yield: 74.3%. mp: 90 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  0.88 (t, 3H), 1.26–1.68 (m, 20H), 2.67 (t, 2H), 5.20 (s, 1H), 6.93 (d, 2H), 7.30 (d, 2H), 7.79 (d, 2H), 7.86 (d, 2H).

Similarly **2a**, **2b**, **2d**, and **2e** were synthesized.

**2a.** Yield: 38.5%. mp 81 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  0.94 (t, 3H), 1.31–1.70 (m, 4H), 2.68 (t, 2H), 5.23 (s, 1H), 6.93 (d, 2H), 7.30 (d, 2H), 7.79 (d, 2H), 7.86 (d, 2H).

**2b.** Yield: 57.5%. mp 81 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz):  $\delta$  0.88 (t, 3H), 1.28–1.68 (m, 10H), 2.67 (t, 2H), 5.26 (s, 1H), 6.93 (d, 2H), 7.30 (d, 2H), 7.79 (d, 2H), 7.86 (d, 2H).

(19) Nabeshima, Y.; Shishido, A.; Kanazawa, A.; Shiono, T.; Ikeda, T.; Hiyama, T. *Chem. Mater.* **1997**, *9*, 1480.

(20) Eich, M.; Wendorff, J. H.; Reck, B.; Ringsdorf, H. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 59.

(21) Eich, M.; Wendorff, J. H. *Makromol. Chem. Rapid Commun.* **1987**, *8*, 467.

(22) Ikeda, T.; Horiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Chem. Lett.* **1988**, 1679.

(23) Bobrovsky, A. Yu.; Boiko, N. I.; Shibaev, V. P. *Liq. Cryst.* **1998**, *25*, 393.

(24) Bobrovsky, A. Yu.; Boiko, N. I.; Shibaev, V. P. *Liq. Cryst.* **1998**, *25*, 679.

(25) Boiko, N. I.; Bobrovsky, A.; Shibaev, V. *Mol. Cryst. Liq. Cryst.* **1999**, *332*, 173.

(26) Bobrovsky, A. Yu.; Boiko, N. I.; Shibaev, V. P. *J. Opt. Technol.* **1999**, *66*, 574.

(27) Bobrovsky, A. Yu.; Boiko, N. I.; Shibaev, V. P.; Springer, J. *Adv. Mater.* **2000**, *12*, 16.

(28) Brehmer, M.; Lub, J.; van de Witte, P. *Adv. Mater.* **1998**, *10*, 17.

(29) van de Witte, P.; Galan, J. C.; Lub, J. *Liq. Cryst.* **1998**, *24*, 819.

(30) Tamaoki, N.; Parfenov, A.; Masaki, A.; Matsuda, H. *Adv. Mater.* **1997**, *9*, 1102.

(31) Tamaoki, N.; Kruk, G.; Matsuda, H. *J. Mater. Chem.* **1999**, *9*, 2381.

(32) Kruk, G.; Tamaoki, N.; Matsuda, H.; Kida, Y. *Liq. Cryst.* **1999**, *26*, 1687.

(33) Tamaoki, N.; Matsuda, H.; Takahashi, A. *Liq. Cryst.* **2001**, *28*, 1823.

(34) Tamaoki, N. *Adv. Mater.* **2001**, *13*, 1135.

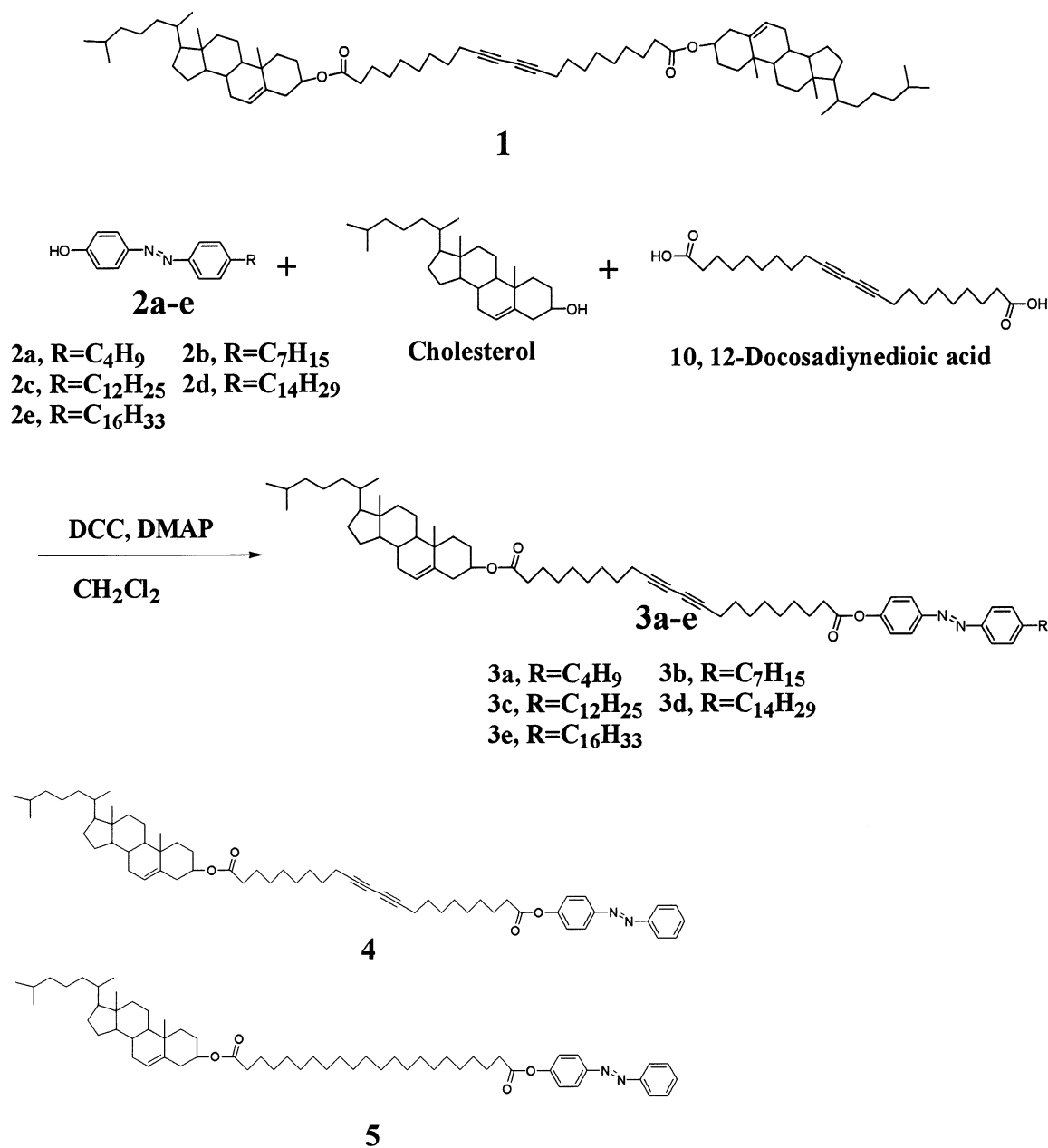
(35) Tamaoki, N.; Song, S.; Moriyama, M.; Matsuda, H. *Adv. Mater.* **2000**, *12*, 94.

(36) Moriyama, M.; Song, S.; Matsuda, H.; Tamaoki, N. *J. Mater. Chem.* **2001**, *11*, 1003.

(37) Moriyama, M.; Tamaoki, N. *Chem. Lett.* **2001**, 1142.

(38) Song, X.; Perlstein, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 9144.

Scheme 1



**2d.** Yield: 38.2%. mp 95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 0.88 (t, 3H), 1.26–1.68 (m, 24H), 2.67 (t, 2H), 5.15 (s, 1H), 6.93 (d, 2H), 7.30 (d, 2H), 7.79 (d, 2H), 7.86 (d, 2H).

**2e.** Yield: 41.3%. mp 99 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 0.88 (t, 3H), 1.25–1.68 (m, 28H), 2.67 (t, 2H), 5.18 (s, 1H), 6.93 (d, 2H), 7.30 (d, 2H), 7.79 (d, 2H), 7.86 (d, 2H).

**3c.** 10,12-Docosadienedioic acid (0.94 g), dicyclohexylcarbodiimide (1.04 g), and 4-(dimethylamino)pyridine (0.045 g) were dissolved in dichloromethane (25 mL) at room temperature. To this solution was slowly added another solution of 4-*n*-dodecyl-4'-hydroxyazobenzene (0.92 g, 2.5 mmol) and cholesterol (0.98 g) in dichloromethane (25 mL) and stirred at room temperature for 24 h. After removal of the precipitate by filtration, the dichloromethane was removed under vacuum, leaving an orange solid. The orange solid was extracted with ether. The ether-soluble part was collected and precipitated from benzene/hexane followed by recrystallization from 2-butanone/hexane to obtain 315 mg of orange crystals. Yield 11.7%. mp 108 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 0.67–2.02 (88H, m), 2.21–2.32 (8H, m), 2.58 (2H, t), 2.68 (2H, t), 4.62 (1H, m), 5.37 (1H, m), 7.22 (2H, d), 7.31 (2H, d), 7.82 (2H, d),

7.94 (2H, d). Anal. Calcd for C<sub>73</sub>H<sub>110</sub>O<sub>4</sub>N<sub>2</sub>: C, 81.21; H, 10.27; N, 2.59. Found: C, 81.36; H, 10.40; N, 2.40.

Similarly **3a**, **3b**, **3d**, and **3e** were synthesized.

**3a.** Yield 13.0%. mp 109 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 0.67–2.02 (78H, m), 2.21–2.32 (8H, m), 2.58 (2H, t), 2.69 (2H, t), 4.61 (1H, m), 5.37 (1H, m), 7.24 (2H, d), 7.32 (2H, d), 7.84 (2H, d), 7.94 (2H, d). Anal. Calcd for C<sub>65</sub>H<sub>94</sub>O<sub>4</sub>N<sub>2</sub>: C, 80.70; H, 9.79; N, 2.90. Found: C, 80.96; H, 9.95; N, 2.70.

**3b.** Yield 9.9%. mp 112 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz): δ 0.67–2.02 (78H, m), 2.24–2.31 (8H, m), 2.58 (2H, t), 2.68 (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<sub>68</sub>H<sub>100</sub>O<sub>4</sub>N<sub>2</sub>: C, 80.90; H, 9.98; N, 2.77. Found: C, 81.04; H, 9.98; N, 2.76.

**3d.** Yield 15.5%. mp 103 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 0.67–2.02 (92H, m), 2.21–2.32 (8H, m), 2.58 (2H, t), 2.68 (2H, t), 4.62 (1H, m), 5.37 (1H, m), 7.21 (2H, d), 7.31 (2H, d), 7.83 (2H, d), 7.94 (2H, d). Anal. Calcd for C<sub>75</sub>H<sub>114</sub>O<sub>4</sub>N<sub>2</sub>: C, 81.32; H, 10.34; N, 2.53. Found: C, 81.18; H, 10.32; N, 2.85.

**3e.** Yield 15.7%. mp 99 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 270 MHz): δ 0.67–2.02 (96H, m), 2.21–2.32 (8H, m), 2.58 (2H, t), 2.68 (2H, t), 4.62 (1H, m), 5.36 (1H, m), 7.21 (2H, d), 7.31 (2H, d), 7.83

(2H, d), 7.94 (2H, d). Anal. Calcd for  $C_{77}H_{118}O_4N_2$ : C, 81.43; H, 10.47; N, 2.47. Found: C, 81.56; H, 10.49; N, 2.49.

**4.** 10,12-docosadiynedioic acid (1.90 g), dicyclohexylcarbodiimide (2.14 g), and 4-(dimethylamino)pyridine (0.12 g) were dissolved in dichloromethane (30 mL) at room temperature. To this solution was slowly added another solution of 4-hydroxyazobenzene (1.03 g) and cholesterol (2.02 g) in dichloromethane (40 mL) and stirred at room temperature for 6 h. After removal of the precipitate by filtration, dichloromethane was removed under vacuum, leaving an orange solid. The crude product was purified by column chromatography using silica gel eluting with a 3:2 mixture of dichloromethane and hexane. A total of 180 mg of orange crystals was obtained after removal of the solvents under vacuum. Yield 3.8%. mp 82 °C.  $^1H$  NMR ( $CDCl_3$ , 600 MHz):  $\delta$  0.67–2.02 (65H, m), 2.24–2.31 (8H, m), 2.59 (2H, t), 4.62 (1H, m), 5.36 (1H, m), 7.25 (2H, d), 7.49–7.51 (3H, m), 7.91 (2H, d), 7.96 (2H, d). Anal. Calcd for  $C_{61}H_{86}O_4N_2$ : C, 80.39; H, 9.51; N, 3.07. Found: C, 80.24; H, 9.74; N, 2.96.

By a similar method for the synthesis of **4**, the compound **5** was synthesized using docosanedioic acid instead of 10,12-docosadiynedioic acid. Yield 5.4%. mp 104 °C.  $^1H$  NMR ( $CDCl_3$ , 270 MHz):  $\delta$  0.67–2.02 (77H, m), 2.24–2.32 (4H, m), 2.59 (2H, t), 4.60 (1H, m), 5.37 (1H, m), 7.25 (2H, d), 7.47–7.55 (3H, m), 7.91 (2H, d), 7.96 (2H, d). Anal. Calcd for  $C_{61}H_{94}O_4N_2$ : C, 81.43; H, 10.47; N, 2.47. Found: C, 81.56; H, 10.49; N, 2.49.

## Results and Discussion

**Design and Synthesis.** Several compounds having both azobenzene and cholesterol groups in a single molecule have been synthesized.<sup>39–41</sup> Since compounds synthesized in the early stage have azobenzene and cholesterol groups connected with a short linkage, the molecular structure becomes rigid and mesophases are not observed or are only observed above 135 °C where thermal isomerization of the azobenzene chromophore from cis to trans is so high that not enough cis form that induces a phase transition was photochemically produced. Yelamaggad et al. reported the synthesis of azobenzene/toran/cholesterol trimesogenic liquid crystals with mesophases around 100 °C, but they did not report their photochemical reaction.<sup>42</sup> Recently, George and Das reported the effect of the photochemical isomerization of a doped compound having azobenzene and cholesterol groups connected via an ethylene linkage on the cholesteric pitch of a mixture of cholesteryl oleyl carbonate, cholesteryl chloride, and cholesteryl nonanoate.<sup>43</sup>

We designed new compounds, **3a–3e**, **4**, and **5**, having azobenzene and cholesterol groups connected with an aliphatic chain containing 22 carbons that would decrease the liquid-crystalline temperature to around 100 °C where sufficient photochemical isomerization of the azobenzene group from trans to cis occurs under the intensity of UV light emitted from a mercury lamp against the reverse thermal reaction. In all cases, we condensed the 1:1 mixture of cholesterol and the corresponding hydroxyazobenzene and the corresponding dicarboxylic acids, and isolated the target compounds by recrystallization or column chromatography.

**Table 1. Phase Transition Temperatures and  $\lambda_{\max}$  of Cholesteric Reflection of the Photochromic LC Compounds**

compound	phase transition temperature <sup>a</sup> (°C)	$\lambda_{\max}$ (nm) (temperature (°C))
<b>3a</b>	Cr 79 SmA 109 I I 105 SmA 26 Cr	–
<b>3b</b>	Cr 89 SmA 112 I I 110 SmA 30 Cr	–
<b>3c</b>	Cr 93 SmA 108 I I 105 SmA 70 Cr	–
<b>3d</b>	Cr 96 SmA 103 I I 100 SmA 74 Cr	–
<b>3e</b>	– I 100 SmA 74 Cr	–
<b>4</b>	Cr 70 Sm 76 Ch 82 I I 80 Ch&Sm 36 <sup>b</sup> Cr	696(50), 595(60) 514(70), 463(80)
<b>5</b>	Cr 97 Ch 104 I I 101 Ch 81 Cr	533(88), 515(90) 485(95), 457(100)

<sup>a</sup> I, isotropic phase; Ch, cholesteric phase; SmA, smectic A phase; Sm, smectic phase; Cr, crystal. <sup>b</sup> A broad signal was observed. Ch–Sm and Sm–Cr transitions could not be separated.

**Table 2. Smectic Layer Spacing  $d$  for Compounds (**3a–3e**) at 95 °C and the Estimated Molecular Length  $L$  in an All Trans Conformation**

compounds	$d$ (Å)	$L$ (Å)
<b>3a</b>	27.9	58
<b>3b</b>	29.7	62
<b>3c</b>	31.8	68
<b>3d</b>	33.7, 55.1	71
<b>3e</b>	34.2, 56.6	73

**Liquid-Crystalline Property.** Table 1 shows the results of the phase transitions of **3a–3e**, **4**, and **5** observed using a polarized optical microscope and differential scanning calorimetry. Compounds without an alkyl chain on the azobenzene group, **4** and **5**, have a cholesteric phase showing a Grandjean planar texture with colors. Compound **4** also has a smectic phase showing a fan-shaped texture at lower temperature. Five compounds with an alkyl chain from butyl to hexadecyl show only the smectic A phase as a mesophase. This was verified by observation of the coexistence of the focal conic fan and homeotropic textures and sharp small-angle reflections in the X-ray diffraction. Table 2 summarizes the small-angle reflections for compounds **3a–3e**. The interlayer distances for **3a–3c** were slightly smaller than half of the molecular length estimated by a molecular model. The distances can be explained by a model assuming an intercalated smectic phase that is proposed for some known nonsymmetric dimesogenic liquid crystals.<sup>44–48</sup> For **3d** and **3e**, other reflections corresponding to 55.1 and 56.5 Å, respectively, were observed. The intensity profiles of the X-ray diffraction pattern for **3c** and **3d** at 95 °C were compared in Figure 1. The coexistence of two periodicities has been observed for other nonsymmetric dimesogens and explained as two-dimensional modulated or incommensurate phases. Our observation of two layer spacings for the compounds **3d** and **3e** can be also explained

(39) Ladenburg, K.; Fernholz, E.; Wallis, E. S. *J. Org. Chem.* **1938**, *3*, 294.

(40) Bloom, A.; Hung, P. L. K. *Mol. Cryst. Liq. Cryst.* **1978**, *44*, 323.

(41) Murata, K.; Aoki, M.; Suzuki, T.; Harada, T.; Kawabata, H.; Komori, T.; Ohseto, F.; Ueda, K.; Shinkai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6664.

(42) Yelamaggad, C. V.; Hiremath, U. S.; Shankar Rao, D. S.; Krishna Prasad, S. *Chem. Commun.* **2000**, 57.

(43) George, M.; Das, S. *Chem. Lett.* **1999**, 1081.

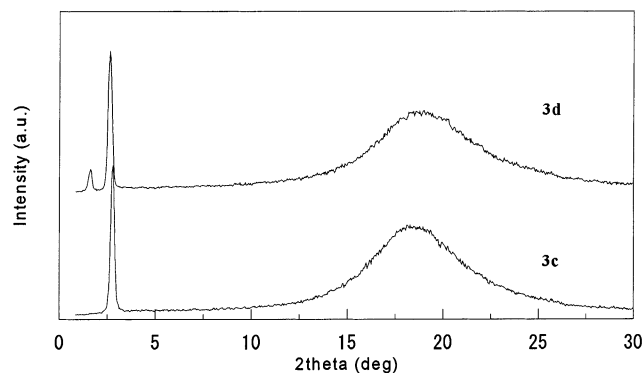
(44) Attard, G. S.; Date, R. W.; Imrie, C. T.; Luckhurst, G. R.; Roskilly, S. J.; Seddon, J. M.; Taylors, L. *Liq. Cryst.* **1994**, *16*, 529.

(45) Blatch, A.; Fletcher, I. D.; Luckhurst, G. R. *Liq. Cryst.* **1995**, *18*, 801.

(46) Masurier, P. J.; Luckhurst, G. R. *Liq. Cryst.* **1998**, *25*, 63.

(47) Masurier, P. J.; Luckhurst, G. R. *Chem. Phys. Lett.* **1998**, *287*, 435.

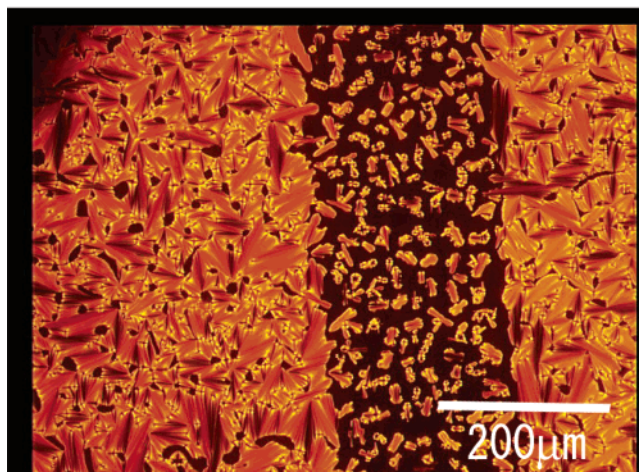
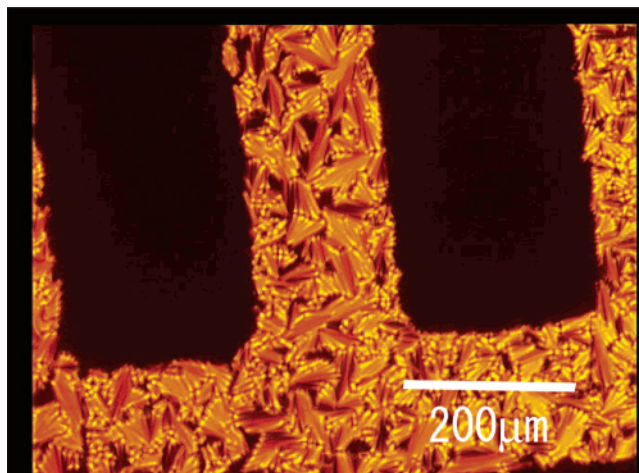
(48) Marcellis, A. T. M.; Koudijs, A.; Klop, E. A.; Sudhölter, E. J. R. *Liq. Cryst.* **2001**, *28* (6), 881.



**Figure 1.** Intensity profiles of the powder X-ray diffraction pattern of the smectic A phase exhibited by compounds **3c** and **3d** at 95 °C.

assuming the above-mentioned phases.<sup>49–52</sup> The fact that the cholesteric phase is observed only for compounds **4** and **5** without an alkyl chain on the azobenzene unit corresponds to the former results for some series of compounds, where the introduction of long alkyl chains enhances the intermolecular interaction in the direction perpendicular to the molecular long axis and stabilizes the smectic phase.<sup>53</sup> Among the compounds with an alkyl chain, only **3e** shows a monotropic phase transition where a smectic phase is observed only upon cooling, while others show the enantiotropic phase transition. Furthermore, **3a** and **3b**, having shorter alkyl chains than the others, showed a large hysteresis, where the liquid-crystalline phase lasts up to 30 °C upon cooling. These results indicate that longer alkyl chains on an azobenzene have the effect of stabilizing a crystalline phase. Comparing compounds **4** and **5** showing a cholesteric phase, **4** having a diacetylene unit shows a liquid-crystalline phase at lower temperature than **5** with a hysteresis where the liquid-crystalline phase lasts up to 36 °C upon cooling. In Table 1, the peak wavelengths of the cholesteric reflection band at various temperatures are shown for compounds **4** and **5**. The reflection bands for both compounds shifted toward a shorter wavelength with increasing temperature ( $d\lambda_{\max}/dT < 0$ ) as observed for the other known cholesteryl esters.

**Photochemical Reaction in Liquid-Crystalline Phase.** If **3a–3e**, **4**, and **5** are irradiated by 366-nm light at their liquid-crystalline temperatures (**3a**, 105 °C; **3b**, 110 °C; **3c**, 102 °C; **3d**, 101 °C; **3e**, 102 °C; **4**, 70 °C; **5**, 100 °C), a phase transition from the birefringent liquid-crystalline to the isotropic phases occurred, which is observed using an optical microscope with cross polarizers (Figure 2 A). The change into the isotropic phase, not into the homeotropic smectic phase, was further confirmed by the absence of the conoscopic cross upon observation of the exposed sample using a Bertrand lens. For the homeotropic texture obtained by



**Figure 2.** Optical textures of the compound **3c** at 98 °C observed after the UV irradiation at 366 nm through a photomask with transparent lines of 200- $\mu\text{m}$  width. (A) Just after the irradiation. The dark area was irradiated. (B) After several tens of seconds.

moving the cover slip, the conoscopic cross was clearly observed in the same but unexposed sample. If the samples showing the isotropic phase after irradiation were kept at the same temperature without 366-nm light irradiation, the original liquid-crystalline phases were recovered (Figure 2B). An azobenzene group exists as the thermally more stable trans form before UV irradiation and stabilizes the liquid-crystalline phase, while after the irradiation, it transforms into cis and destabilizes the liquid-crystalline phase, changing into an isotropic phase. In the dark, an azobenzene group thermally isomerizes from cis to trans, and the compounds return to the original liquid-crystalline states. For compounds **4** and **5** showing a cholesteric phase, a certain amount of shift in the reflection band toward shorter wavelengths is observed during the early stage of the irradiation. Further irradiation induced a phase transition to isotropic. Under 436-nm light at 65 °C, the reflection band of compound **4** gradually shifted from 570 to 480 nm, but a phase transition to isotropic is not observed, even at the photostationary state (Figure 3). Similarly, the reflection band of compound **5** shifted from 558 to 470 nm at 85 °C under 436-nm light. To explain the different results depending on the exposure wavelength, we have to think about two factors, the concentration and concentration distribution of each

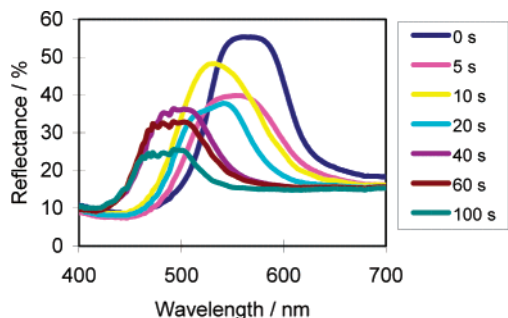
(49) Hardouin, F.; Achard, M. F.; Jin, J.-H.; Yun, Y.-K.; Chung, S.-J. *Eur. Phys. J. B* **1998**, *1*, 47.

(50) Cha, S. W.; Jin, J.-I.; Laguerre, M.; Achard, M. F.; Hardouin, F. *Liq. Cryst.* **1999**, *26* (9), 1325.

(51) Lee, D. W.; Jin, J.-I.; Laguerre, M.; Achard, M. F.; Hardouin, F. *Liq. Cryst.* **2000**, *27* (1), 145.

(52) Lee, J.-W.; Jin, J.-I.; Achard, M. F.; Hardouin, F. *Liq. Cryst.* **2001**, *28* (5), 663.

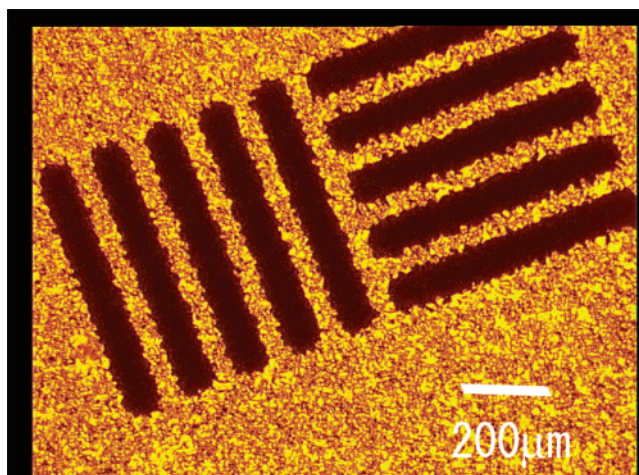
(53) Wiegeleben, A.; Richter, L.; Deresch, J.; Demus, D. *Mol. Cryst. Liq. Cryst.* **1980**, *59*, 329.



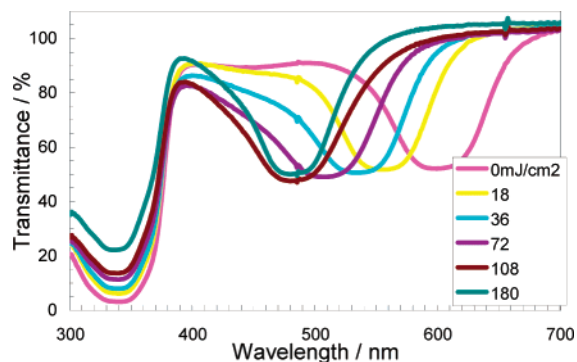
**Figure 3.** Reflection spectra of compound **4** at 65 °C before and after different irradiation times at 436 nm. The thickness of the sample was maintained by sandwiching the mixture between two quartz plates using glass spacers with 10- $\mu\text{m}$  diameter. Reflected light was left-handed circularly polarized. Reflectance over 50% may be due to the reflection of the incident light at the glass plate surfaces.

isomer in the film after irradiation. Azobenzenes without quite polar substituents usually have an intense  $\pi-\pi^*$  and a weak  $n-\pi^*$  transitions. The excitation at either transition band induces the isomerization from trans to cis and from cis to trans. The ratio of the isomers at the photostationary state is determined by the quantum yield of each photochemical route and the absorbance of the isomers. Usually the irradiation at the  $\pi-\pi^*$  transition band forms more cis isomer because of the larger absorbance for the trans isomer. The compound **4** showed  $\pi-\pi^*$  and  $n-\pi^*$  transitions at 326 and 444 nm, respectively, in chloroform. The molar absorption coefficient of the compound at 366 and 436 nm were 4066 and 743  $\text{mol}^{-1} \text{cm}^{-1}$ , respectively. By the observation of the absorbance change in chloroform, it was determined that more than 90% and <20% of the molecules is changed from trans to cis by 366- and 436-nm irradiations, respectively. So one of the possible reasons for the different results for the film depending on the irradiation wavelength can be the different concentration of the cis isomer after the photoreaction. Another possibility is the inhomogeneous formation of the cis isomer at 366 nm. The film of the compounds with a thickness of about 10  $\mu\text{m}$  has an absorbance over 3 at 366 nm, so the rate of the photoreaction between the two surfaces becomes quite different, which induces an inhomogeneous concentration of the cis form of azobenzene in the direction of the thickness. By changing the irradiation wavelength from 366 to 436 nm, the absorbance becomes <1 and the concentration of the cis form at the photostationary state becomes lower, which results in the rather homogeneous production of the cis isomer within the concentration that does not induce the phase transition for compound **4**.

**Fixation of the Phases in the Glassy State.** The molecular alignment of compounds **3a–3e**, **4**, and **5** at their liquid-crystalline temperature before and after irradiation was fixed in the glassy state by rapid cooling to 0 °C. The glassy state obtained by cooling was stable at room temperature for all compounds, and no effect on the molecular alignment is observed, even after UV irradiation in the glassy state. Upon heating to its isotropic temperature, the glass is completely melted. While the compound was kept at its isotropic temperature in the dark for a some time, even the irradiated sample began to show the same phase transition temperature as the sample without irradiation. This may



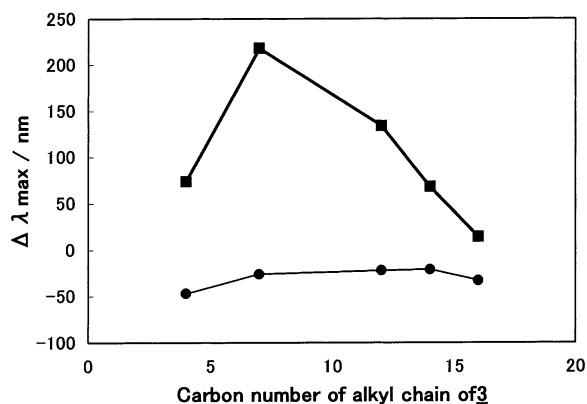
**Figure 4.** Optical textures of the compound **3c** at room temperature observed after UV irradiation at 366 nm through a photomask with transparent lines of 65- $\mu\text{m}$  width at 98 °C followed by quenching by dipping the sample into ice-water.



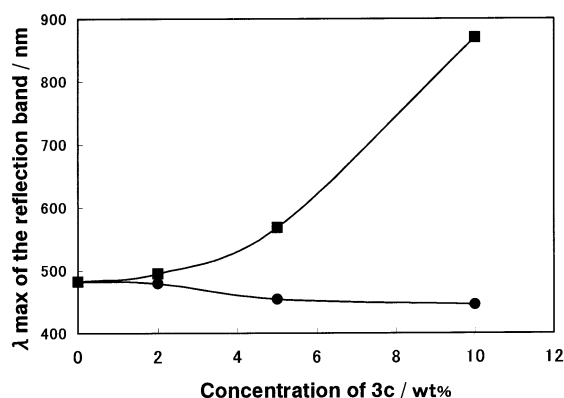
**Figure 5.** Transmission spectra of the mixture of compounds **1** and **3b** (3 wt %) at 92 °C before and after different UV irradiation times. The thickness of the sample was 10  $\mu\text{m}$ .

be due to the thermal isomerization of the azobenzene group from cis to the more stable trans form. If the thin film of samples **3a–3e** between thin glass plates is irradiated with 366-nm light through a photomask at a temperature around 2 °C below the isotropic–smectic transition and rapidly cooled, a pattern with dark and light areas observable under cross polarizers was fixed (Figure 4). The dark and light areas correspond to the isotropic and smectic parts attained after and without UV irradiation, respectively. For compounds **4** and **5**, a pattern with different cholesteric reflection colors was fixed by imagewise irradiation at 436 nm at their liquid-crystalline temperature followed by rapid cooling.

**Effect as Dopants for Dicholesteryl Esters Forming a Stable Glass.** To evaluate the compounds with both cholesterol and azobenzene groups as a photoresponsive dopant in glass-forming cholesteric liquid crystals, the thin film of **1** containing **3a–3e** at 2–10 wt % were prepared. The reflection bands for the thin films of the mixture were measured after fixing in the glassy state obtained by rapid cooling from their liquid-crystalline temperatures to 0 °C with or without irradiation. When **3c** was doped in **1**, the reflection band was shifted toward longer wavelengths at 95 °C. After the irradiation with 366-nm light to the photostationary state, the reflection band shifted toward a wavelength shorter than pure **1** (Figure 5). Depending on the alkyl chain on the azobenzene of the dopants, the degree of



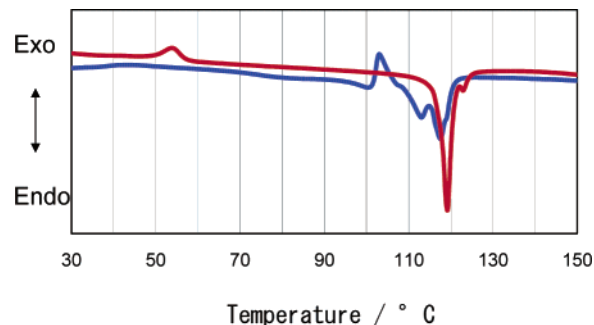
**Figure 6.** Change in  $\Delta \lambda_{\max}$  of the films 5 wt % of **3a–3e** as a function of carbon number of the substituted alkyl chain on the azobenzenes (*n*) at 90 °C. Square: before irradiation of the films including (*E*)-azobenzenes. Circle: after irradiation of the films at 366 nm (*Z* form is enriched).



**Figure 7.** Change in  $\lambda_{\max}$  as a function of the concentration of **3c** at 95 °C. Square: before irradiation of the films including (*E*)-**3c**. Circle: after irradiation of the films at 366 nm (*Z* form is enriched).

the shift in the reflection band upon doping was changed. In Figure 6, the shift from pure **1** of the reflection band before and after the UV irradiation is plotted versus the carbon number in each alkyl chain. The curve has a peak around the heptyl group. Such an effect of the alkyl chain length in the cholesterol–azobenzene dimesogenic dopants on the reflection band is similar to that in a series of dialkylazobenzenes shown in a former study. Figure 7 shows the dependence of the dopant concentration on the amount of the shift in the reflection band. The shift in the reflection band is increased by increasing the concentration of the dopant but not in a monotonic manner.

Some effects of the photochemical reactions on the cholesteric pitch have been reported for various combinations of host liquid crystals and photoresponsive dopants. One of the effects is the twisting power change of the dopant upon the photochemical reaction.<sup>17,54</sup> This effect is observed only for the chiral photoresponsive dopant. Another effect is the change in the phase transition temperature of the mixture.<sup>8</sup> If the phase transition temperature is shifted upon photoreaction, the reaction induces a similar effect to the temperature change that sometimes causes a large pitch shift. The



**Figure 8.** DSC thermograms of compound **1** containing 5 wt % of **3c** (blue line) or 4,4'-di-*n*-dodecylazobenzene (red line). The measurements were done upon heating for the glassy samples quenched from their cholesteric temperatures.

last effect is the formation of the smectic clusters in the cholesteric phase. The molecules in the smectic clusters align parallel to each other without twisting, so the cholesteric pitch is elongated as the number and size of the cluster increased. This effect has been reported for explaining the cholesteric pitch change upon temperature change for the mixtures of cholesterol derivatives or an achiral biphenylcyclohexane derivative containing chiral additives.<sup>55–57</sup>

Our dopants are chiral, but the chiral cholesterol unit is apart from the photoresponsive azobenzene unit. So it is difficult to consider that the twisting powers for the dopant in the *trans* and *cis* forms are so different. And we have observed a similar effect of the cholesteric pitch shift by doping the achiral 4,4'-di-*n*-dodecylazobenzene to the same host liquid crystal.<sup>36</sup> We also confirmed that the addition of **3b** in the *trans* form up to 5 wt % concentration, which induced a very large shift of the cholesteric pitch, causes no effect on the phase transition temperature of **1**. We think that our results can be well explained by the formation of the smectic domain in the cholesteric phase of **1** induced by doping of the photoresponsive dopant in the *trans* form and the destruction of it by the photochemical isomerization of the dopant from *trans* to *cis*. The suitable length of an alkyl chain on the azobenzene unit of the dopant may be needed to stabilize the smectic layer in the cholesteric phase of the host liquid crystal. This must be the reason we see the unusual maximum of the shift of the wavelength of the reflected light in Figure 6. And the bent structure of the *cis*-azobenzene unit of the dopant obtained after the photoisomerization may not work as the stabilizer for the smectic order formation in the cholesteric phase. The experimental works using X-ray diffraction for verifying the proposed mechanism are underway.

To estimate the thermal stability of the glassy state of **1** containing **3c**, we compare the DSC measurements for the samples of **1** containing **3c** and **1** containing a 4,4'-di-*n*-dodecylazobenzene. If the measurement started from the glassy state, the latter showed a glass transition temperature around 45 °C, whereas the former did not show an apparent glass transition up to the exotherm at 104 °C for crystallization (Figure 8). These results correspond to the observation of the color change

(55) Voss, J.; Sackmann, E. *Z. Naturforsch.* **1973**, *28A*, 1496.

(56) Chen, S.-H.; Wu, J. J. *Mol. Cryst. Liq. Cryst.* **1982**, *87*, 197.

(57) Ania, F.; Stegemeyer, H. *Mol. Cryst. Liq. Cryst. Lett.* **1985**, *2*, 67.

(54) van Delden, R. A.; Koumura, N.; Harada, N.; Feringa, B. L. *Proc. Natl. Acad. Sci.* **2002**, *99*, 4945.

of the sample on the temperature-controlled hot stage. The improvement of the thermal stability of the glassy state with the cholesteric reflection would make it possible to practically apply this system to color-recording materials working in a photon mode.

**Photochemical Recording Using the Mixture of Dicholesteryl Ester and 3.** The properties of the mixture of the dicholesteryl ester and azobenzene derivatives **3a–3e** enable us to realize rewritable full-color recording in photon mode. By irradiation of the thin film of the mixture at its cholesteric temperature between a pair of glass plates with 325-nm light from a He–Cd laser equipped with a modulator and a galvanoscanner, a color image serving as a jpeg file was directly reproduced and fixed in the cholesteric film by the following cooling process. A fixed image obtained by the laser recording system is shown in Figure 9. The image was completely stable at room temperature under room light for at least 1 year. It disappeared by heating the sample above 130 °C, and a new image was recorded by irradiation at 93 °C followed by cooling to 0 °C.

### Conclusion

The dimesogenic compounds having both cholesterol and azobenzene groups show only a smectic or a cholesteric phase or both smectic and cholesteric phases depending on the presence of the alkyl chain on the photoresponsive mesogen and a diyne group in the spacer connecting the two mesogens. Upon UV irradiation at liquid-crystalline temperature, these liquid-crystalline compounds showed a phase transition from smectic or cholesteric to isotropic or a shift in the wavelength of the cholesteric reflection band, triggered by photochemical isomerization of the azobenzene group from the trans to cis isomer. By rapid cooling to 0 °C, the molecular order for both the irradiated and nonirradiated samples were fixed in the glassy state, which was stable at room temperature. If compounds with both cholesterol and azobenzene groups are doped in a



**Figure 9.** Color picture recorded using the laser scanning system in the thin film of the mixture of **1** and **3c** (5 wt %).

dicholesteryl compound forming a stable cholesteric glass, the shift in the reflection band toward a longer wavelength was observed. The effect of the doping on the reflection band significantly depended on the length of the alkyl chain on the azobenzene group of the dopant, maximizing at the heptyl group. The thermal stability of the glassy state maintaining the cholesteric color of the dicholesteryl compound was higher with the photoresponsive dopant having a cholesteryl group than the dialkylazobenzene. These photochemical and thermal properties of the photoresponsive liquid crystal or liquid-crystalline mixture can be used for rewritable recording materials.

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