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Effects of doped dialkylazobenzenes on helical pitch of cholesteric liquid crystal with medium molecular weight: utilisation for full-colour image recording

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The effects of small amounts of achiral photochromic dopants, 4,4′-di-*n*-alkylazobenzenes, with various lengths of substituted alkyl chain (C_nH_{2n+1} : $n = 4$, 7, 11, 12, 13, 14, 15, 16) on the helical pitch of a cholesteric liquid crystal (CLC) with *ca.* 1000 molecular weight were investigated in order to utilise the cholesteric reflected colour of these combinations for a rewritable colour image recording. The *(E)*-azobenzenes (~2 wt%) in the host CLC induced pitch changes dependent on temperature, the concentration of the azobenzenes and the length of substituted alkyl chain on the azobenzenes. In the low region of the cholesteric temperature (below 100 °C), some *(E)*-azobenzenes remarkably lengthened the pitch. Contrary to this, upon irradiation, *E*–*Z* photoisomerization of all the azobenzenes in the CLC phase induced consecutive pitch shortenings in response to the formation of the *Z* isomers. The changed pitch (reflected colour) could be fixed in cholesteric glassy solids. In the glassy solid state, the photo and thermal isomerization of the azobenzenes could not influence the cholesteric pitch any longer, therefore, the colour was stably stored. However, since the molecular arrangement of the CLC and the conformation of the doped azobenzenes completely returned to the initial state upon re-heating to isotropic temperatures, the stored colour could be easily erased. Based on these fundamental investigations, it is suggested that the mixed systems of the medium-molecular-weight CLCs and the 4,4′-dialkylazobenzenes will be effective materials for a rewritable full-colour image recording in a photon mode.

Introduction

Since the optical properties of liquid crystals (LCs) respond to internal or external environment, special attention has been paid to their applications. Among the LCs, the cholesteric liquid crystal (CLC) has a characteristic optical property of reflecting one circularly polarised component of light, whose wavelength (λ) corresponds to the product of the pitch (P) and the average of the refractive index (n).

$$\lambda = nP$$

When λ is in the visible region, the CLC shows an iridescent reflected colour. The reflected colour (cholesteric pitch) is influenced by the temperature, external force, magnetic field, electric field and chemical compositions.[1] From the viewpoint of the pitch change due to the modification of the chemical compositions in mixed CLC systems, many studies have been carried out for various kinds of mixed systems.[1–5] Among these, the change in the helical pitch caused by photochemical reactions in the CLCs is especially of interest.[3–5] As a result of the fact that the photochemical reactions alter the composition of the CLCs, the cholesteric pitch changes. Adams and Haas investigated the pitch change of cholesteryl nonanoate–cholesteryl iodide by UV irradiation.[4] Upon irradiation, the photodecomposition of cholesteryl iodide reduced the ratio of itself in the mixed system, thus resulting in a cholesteric pitch change. In the studies concerning the effect of small amounts of photochromic dopants, Sackmann reported the pitch changes induced by reversible photochemical reactions such as the photoisomerizations of azobenzene and stilbene in the CLC (mixture of cholesteryl chloride and cholesteryl nonanoate).[5] Their studies revealed the possibility of writing optical information by irradiation initiating the photochemical reactions of photoreactive components and reading the information from the changed reflection of the CLCs. On the other hand, the fluidity of the liquid crystalline phase is a disadvantage for the storage of the static information without energy to keep the molecular alignment. In order to stably store the information, CLC polymers or macromolecules, which form a glassy solid that maintains the helical structure,[6] would be appropriate.

Recently, we reported the thermal and optical properties of dicholesteryl compounds with *ca.* 1000 molecular weight which was almost the highest among the low-molecular-weight CLCs.[7] They show CLC phases with reflected colours, which quickly respond to temperature and are fixed in a glassy state by rapid cooling from the CLC phases. Since the glass transition temperature of these compounds is *ca.* 80 °C, the fixed colour is stably maintained at room temperature. Although a low-molecular-weight CLC shows a higher rate of molecular alignment in the CLC phase than a polymeric CLC, it can not generally form the glassy solid stable at ambient temperature. The molecular weight of our CLC compounds is one of the important factors for attaining both the properties of a quick response of the reflected colour to temperature in the CLC phase and the stable cholesteric structure in the glassy solid state. Accordingly, we defined our compounds as "medium-molecular-weight" CLCs and expected that they were suitable for fast writing and stable storage of optical information due to the cholesteric reflected colours.

Thus, at first, our attentions were focused on whether or not the photochemical reactions induced the pitch changes in the

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medium-molecular-weight CLCs and whether or not the mixed systems consisting of the CLCs and photoreactive dopants formed stable glassy solids that keep the cholesteric structure, because we would like to apply them for new recording materials.[8] In this study, achiral 4,4′-di-*n*-alkylazobenzenes (number of carbon atoms in the substituted alkyl chain, $n=4$, 7, 11, 12, 13, 14, 15, 16) having a high solubility in the medium-molecular-weight CLCs were employed as photoreactive dopants. Interestingly, while investigating the pitch change by the addition of *E*-4,4′-di-*n*-alkylazobenzenes to the host CLC, a peculiar behaviour of the changed pitch was observed. The achiral *E*-azobenzenes with suitable lengths of the substituted alkyl chain remarkably lengthened the pitch in the region of low CLC temperature, though their concentrations were only ~2 wt%.

In this article, we present the investigations on the effects of small amounts of doped 4,4′-di-*n*-alkylazobenzenes with various lengths of substituted alkyl chain on the cholesteric pitch (reflected colour) in the CLC phase and glassy solid state. At the end of this article, we also introduce a possibility of a repetitive colour image recording in a photon mode with the combination of the medium-molecular-weight CLC and the achiral dialkylazobenzenes.

Results and discussion

Host CLC and guest photoreactive molecules

The structure and the thermal properties of the host CLC compound, the azobenzene derivatives and the mixed CLCs used in this work are summarised in Scheme 1 and Table 1, respectively. Dicholesteryl docosa-10,12-diynoate (**1**) was designed and synthesised as a CLC compound to have both a high enough reorientation rate of molecular ordering in the cholesteric liquid crystalline phase and sufficient molecular ordering stability at room temperature in the cholesteric glassy state obtained after rapid cooling from the liquid crystalline phase.[7] The dicholesteryl ester **1** shows the CLC phase with iridescent colours at its cholesteric temperature. The photochromic dopants, 4,4′-di-*n*-alkylazobenzenes (substituted alkyl chain: C_nH_{2n+1}) used in this study, which include the already known compounds (**2a** ($n=4$) and **2b** ($n=7$)) and unknown ones (**2c**–**2h** ($n=11$–16)), have a variety of properties as shown in Table 1.[9,10] All the azobenzenes can be easily dissolved in the host cholesteric **1**, which do not induce a particular change in the thermal properties of **1** since their concentration is low. All the azobenzenes in **1** photochemically converted from the *E* to *Z* isomer and photochemically or thermally from the *Z* to *E* isomer. We then examined the effects of small amounts of doped **2a**–**2h** on the cholesteric reflection. As to the cause of the change in the reflection induced by the doped azobenzenes, the following three possibilities are considered from the relation, $\lambda=nP$; (1) the change in refractive index, (2) the change in helical pitch, (3) the combination of both. However, the change in refractive index induced by adding small amounts of azobenzenes to polymer or LC materials and by their isomerization is generally small.[11] In these studies, the change in refractive index is up to *ca.* 0.7% ($\Delta n=0.01$, $n=1.5$), though the change in the reflection observed in the present study amounts to *ca.* 50% ($\Delta\lambda_{\max}=250$, $\lambda_{\max}=500$). Hence, it is obvious that the change in the reflection is mainly ascribable to the change in helical pitch.

Table 1 Liquid crystalline properties of employed materials[a]

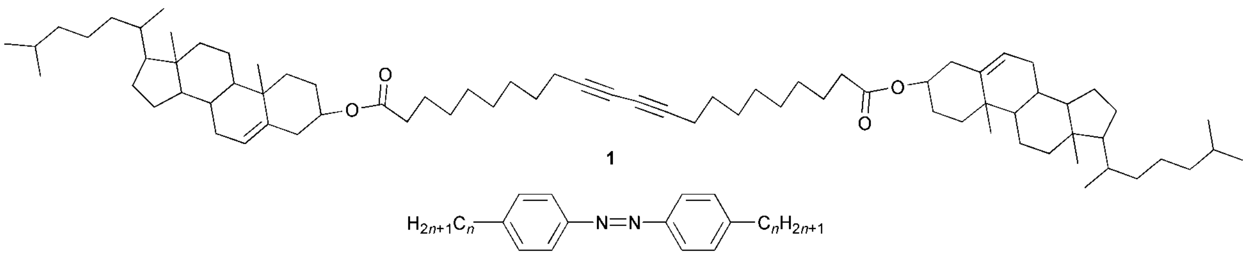
Material	M.W.	Transition temperature/°C
1	1099	117(I→Ch), 82(Ch→Cr)[b]
2a	294	25–27.5(I→Cr, no mesophase)[c]
2b	379	46–46.5(I→N), 39.5–40.5(N→Cr)[c]
2c	491	60(I→N), 56(N→Sm), 36(Sm→Cr)[d]
2d	519	60(I→Sm), 51(Sm→Cr)[d]
2e	547	65(I→Sm), 51(Sm→Cr)[d]
2f	575	62(I→Cr, no mesophase)[d]
2g	603	69(I→Sm), 60(Sm→Cr)[d]
2h	631	70(I→Cr, no mesophase)[d]
2a/1(2 wt%)	—	115(I→Ch), 78(Ch→Cr)
2b/1(2 wt%)	—	115(I→Ch), 78(Ch→Cr)
2c/1(2 wt%)	—	115(I→Ch), 79(Ch→Cr)
2d/1(2 wt%)	—	114(I→Ch), 77(Ch→Cr)
2e/1(2wt%)	—	116(I→Ch), 81(Ch→Cr)
2f/1(2 wt%)	—	115(I→Ch), 81(Ch→Cr)
2g/1(2 wt%)	—	115(I→Ch), 79(Ch→Cr)
2h/1(2 wt%)	—	116(I→Ch), 82(Ch→Cr)

[a]Cr: crystal, Ch: cholesteric phase, N: nematic phase, Sm: smectic phase, I: isotropic phase. [b]Ref 7*b*. [c]Ref. 9. [d]Ref 10.

Effects of *(E)*-4,4′-dialkylazobenzenes on cholesteric pitch

The samples of the dicholesteryl ester **1** containing ~2 wt% of *(E)*-**2a**–**2h** were melted between glass or quartz plates above 120 °C, and cooled to 87–115 °C to obtain thin films (*ca.* 10 μm) in the light-reflecting CLC phase. All the mixtures showed only the cholesteric phase as the mesophase, which was confirmed by differential scanning calorimetry (DSC) measurements and microscope observations (Table 1). After the films gave the CLC phase with reflected colour, they were dipped in an ice bath (*ca.* 0 °C) to obtain glassy solid films retaining the reflected colour of the CLC phase. The reflection bands were measured at room temperature for these glassy solid films.

Fig. 1 shows the correlation between the wavelength of the maximum reflection ($\lambda_{\max}$) and temperature for the films containing 2 wt% of *(E)*-**2a**–**2h** in **1** (black circles). For all the films, $\lambda_{\max}$ decreased (the pitch shortened) with an increase in temperature, which was similar to the behavior of pure **1** (white triangles).[7] However, the addition of the *(E)*-azobenzenes induced shifts of $\lambda_{\max}$ from $\lambda_{\max(0)}$ ($\lambda_{\max}$ of pure **1**), whose extent was quite dependent on the added azobenzenes and the temperature. Below 100 °C, $\lambda_{\max}$ of the cholesteric films containing *(E)*-**2b**, **2c**, **2d**, **2e**, **2f** and **2g** shifted to longer wavelength (red shift and the pitch lengthened) in comparison with that of pure **1**, while $\lambda_{\max}$ of the films with *(E)*-**2a** and **2h** slightly shifted to shorter wavelength (blue shift and the pitch shortened). The red shifts below 100 °C expanded non-linearly with a decrease in the temperature and amounted to 200 nm in some cases. Further, it was revealed that the red shifts



Scheme 1

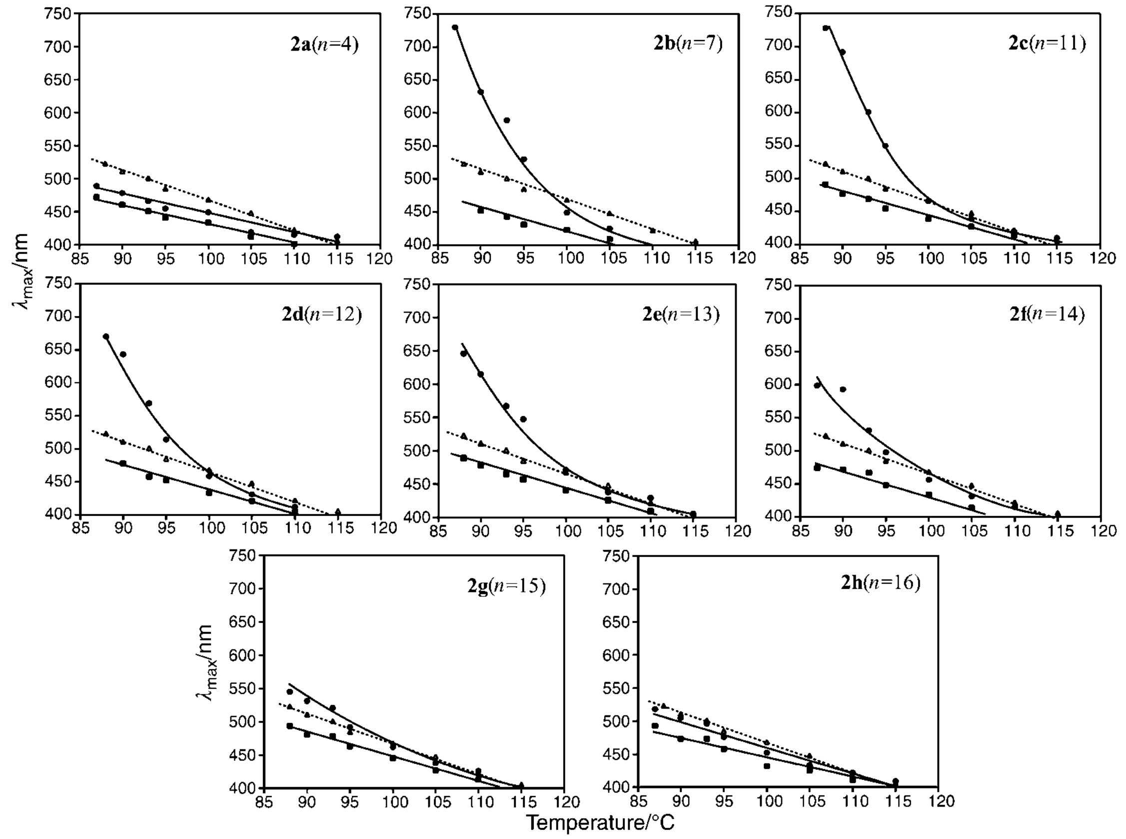


Fig. 1 Correlations between cholesteric temperatures and λ_{max} of reflection bands of the cholesteric films containing 2 wt% of **2a**–**2h** in **1**. Black circles: before irradiation at 366 nm (the effect of *(E)*-azobenzenes); black squares: after irradiation at 366 nm (the effect of *(Z)*-azobenzenes); white triangles: λ_{max} of pure **1**.

expanded non-linearly with an increase in the concentration of the azobenzenes as shown in Fig. 2 by plotting $\Delta\lambda_{max}$ ($\lambda_{max}-\lambda_{max(0)}$) *versus* the concentration of the azobenzenes in the case of **2d** doped in **1** at 93 °C (black circles). In contrast to this, λ_{max} of the samples containing *(E)*-**2a** and **2h** linearly changed with the temperature (Fig. 1) and the concentration (white circles in Fig. 2), and the amounts of their shifts were 30 nm at most. On the other hand, remarkable differences in the band shifts among the samples with *(E)*-**2a**–**2h** were not observed above 100 °C. For all the samples, λ_{max} changed linearly with temperature and their values were always lower or almost same in comparison with that of pure **1**. These dependences of the change in λ_{max} on the dopants and temperature are summarized in Fig. 3 by depicting $\Delta\lambda_{max}$ of the cholesteric films prepared at 90 and 105 °C as a function of carbon number (n) of the substituted alkyl chain (C_nH_{2n+1}) on **2a**–**2h**. The values at 90 °C (black circles) have a maximum for $n=11$(**2c**), while those at 105 °C (white circles) have hardly any differences among all the alkyl chain lengths. From these results along with the data described in Table 1, the band shifts below 100 °C would not be attributed to the molecular weight, thermal properties or odd–even effect of the substituents on the doped azobenzenes but to the chain length of the substituted alkyl groups. Such dependence and large pitch change were not observed in the case of *n*-alkanoic acid, *n*-alkane, and *n*-alkanol doping in steroid cholesterics.[2k] Moreover, the reports on the influence of nematic molecules with various alkoxy lengths, *N*-

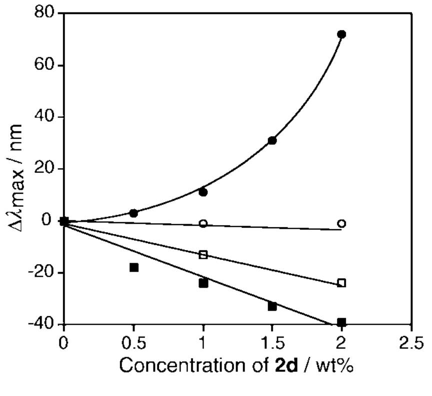


Fig. 2 The change in $\Delta\lambda_{max}$ as a function of the concentration of **2d** at 93 and 105 °C. Black circles: before irradiation of the films including *(E)*-**2d** at 93 °C; black squares: after irradiation of the films at 366 nm at 93 °C (*Z* form is enriched); white circles: before irradiation of the films including *(E)*-**2d** at 105 °C; white squares: after irradiation of the films at 366 nm at 105 °C (*Z* form is enriched).

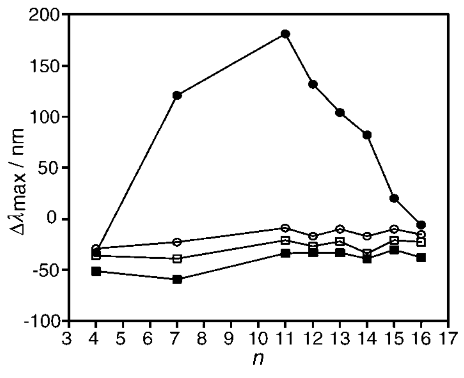


Fig. 3 The changes in $\Delta\lambda_{max}$ of the films including 2 wt% of **2a**–**2h** as a function of carbon number of the substituted alkyl chain on the azobenzenes (n) at 90 and 105 °C. Black circles: before irradiation of the films including *(E)*-azobenzenes at 90 °C; black squares: after irradiation of the films at 366 nm at 90 °C (*Z* form is enriched); white circles: before irradiation of the films including *(E)*-azobenzenes at 105 °C; white squares: after irradiation of the films at 366 nm at 105 °C (*Z* form is enriched).

p-alkoxybenzilidene-*p*-butylaniline (from methyloxy to decyloxy), in steroid cholesterics on the helical pitch did not show a similar dependence.[2h]

The dependence of the cholesteric pitch on the alkyl chain length and the temperature, observed in this study, would be caused by the difference in the interaction between each azobenzene and the host CLC. This interaction is probably due to the arrangement of the azobenzenes in the CLC. It is presumed that below 100 °C *(E)*-**2c** can align most appropriately to lead this interaction, and the increase or decrease in alkyl chain length displaces the arrangement of the doped azobenzenes from the most appropriate position in the CLC. The azobenzenes *(E)*-**2a** and **2h** can not align in a similar manner as *(E)*-**2b–2g**, and as a result the pitch lengthening would not occur and the slight pitch shortening induced by the intrinsic properties of the azobenzenes as normal achiral impurities would result. Further, above 100 °C an increase in molecular motion and a decrease in viscosity of the CLC matrix would displace the arrangement of all the azobenzenes from the arrangement influencing the pitch lengthening. As the result, the intrinsic property of the azobenzenes as impurities would mainly make the pitch slightly shorter for all the mixtures. The normal impurities only disorder the molecular arrangement. Hence, the effect of the normal impurities on the cholesteric pitch should be analogous to that of the thermally induced disordering. In this case, that effect is for pitch shortening, which is similar to that of the *(Z)*-azobenzenes described in the next section.[3f]

It is widely known that addition of chiral molecules to nematic or cholesteric liquid crystals induces appearance or modification of the CLC phase. It would be easy to understand such phenomena, because a macroscopic chirality of CLC is caused by a microscopic chirality of constituent molecules. On the other hand, it was also observed that anomalous modifications of the helical pitch were induced by some mixed achiral molecules.[2g–2i,2m,2n,5] One interpretation, that the smectic type molecular arrangement participates in the anomalous pitch change, has been suggested.[2g,2n] For our mixed samples, although the smectic phase was not observed, the addition of the appropriate *(E)*-azobenzenes might increase the lateral intermolecular interaction and bring the partial molecular alignment close to the smectic type. Meanwhile, the possibility of the induction of structural chirality in an asymmetric field such as CLC can not be disregarded completely. For our present results that the addition of *(E)*-**2b–2g** to **1** made the pitch remarkably longer, it seemed as if the achiral azobenzenes had a strong and opposite twist power compared with that of **1**. There has been a report that *(E)*-diaryl molecules such as *(E)*-stilbene oxide which could form an asymmetric structure had a high twisting power.[12] Accordingly, there might be the possibility that the *(E)*-azobenzenes can form asymmetric conformations in an asymmetric field such as a CLC matrix.

In this study, we revealed that even the addition of small amounts of the achiral azobenzenes with suitable alkyl chains could dramatically expand the spectral region of the reflected colour of medium-molecular-weight CLCs, though we could not specify the reason for the anomalous pitch changes.

Pitch changes by photoisomerization of 4,4′-dialkylazobenzenes in the CLC phase

The change in the cholesteric pitch (cholesteric colour) by the *E–Z* photoisomerization of doped **2a–2h** was also investigated. While maintaining the liquid crystalline temperature, the films consisting of **1** and *(E)*-**2a–2h** between glass or quartz plates were irradiated with a 366 nm light from a high pressure mercury lamp passed through appropriate filters. The irradiation caused the photoisomerization of **2a–2h** from the *E* to *Z* isomer, which induced λ_{max} to become lower values (the pitch shortened and the reflected colour shifted to blue). After the irradiation at the CLC phase, the films were rapidly cooled to 0 °C, which produced the glassy solid films that maintained the CLC molecular alignment (reflected colour).

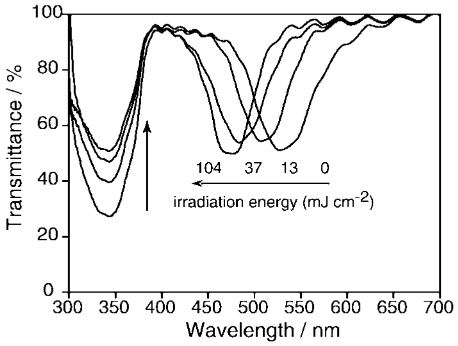


Fig. 4 Transmission spectra of the films of **1** including 1 wt% of **2d**. Four solid films were prepared by dipping the mixture between two glass plates into ice–water after irradiation at 366 nm with different energies, controlled by the irradiation time, at 90 °C.

Depending on the irradiation energy, the reflected colour was changed as shown in Fig. 4 which shows the transmission spectra of the glassy solid films obtained by changing the irradiation energy in the case of **1** containing 1 wt% of **2d**. The bands in the visible region with about 50% transmittance in the figure are for the reflection due to the helical molecular ordering with the axis perpendicular to the substrate. Another band in the ultraviolet region is the absorption due to the π–π* transition of **2d**. In Fig. 5, the ratio for *(Z)*-**2d**, which is estimated from the absorbance at 344 nm assuming that the extinction coefficient for *(Z)*-**2d** is negligible in comparison with that for *(E)*-**2d**, and λ_{max} for the reflection band are plotted *versus* the exposure energy. The λ_{max} for the reflection band shifted to lower wavelength with an increase in the *Z* ratio. Additionally, the increase in the amount of the azobenzenes further shortened the pitch, which was revealed by the concentration effect of the azobenzenes as shown in Fig. 2 (black squares), where the amount of the *Z* isomer in the photostationary state after 366 nm irradiation increased with an increase of the starting concentration in the *(E)*-azobenzenes in **1**. For all the azobenzenes **2a–2h**, the effects of the *Z* isomers on the cholesteric pitch are described in Fig. 1 (black squares) and Fig. 3 (black and white squares). From the figures, it is confirmed that all the *(Z)*-azobenzenes have the property of shortening the cholesteric pitch from those of the mixtures including *(E)*-azobenzenes and of pure **1**. The reason why the *(Z)*-azobenzenes shorten the pitch would be that the *Z* isomers only disorder the molecular arrangement of the CLC phase because of their bent structures and the pitch changes to the disordered sense. In this case, the disordered sense is for shortening pitch because the thermal behaviour of the host **1**

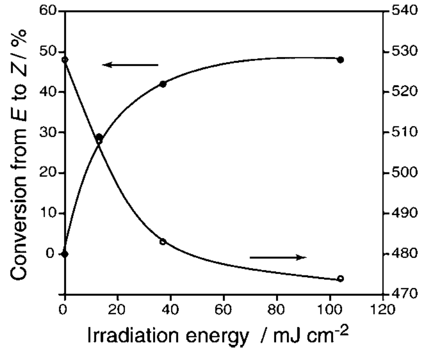


Fig. 5 Plots of λ_{max} of reflection band and conversion from *E* to *Z vs.* irradiation energy.

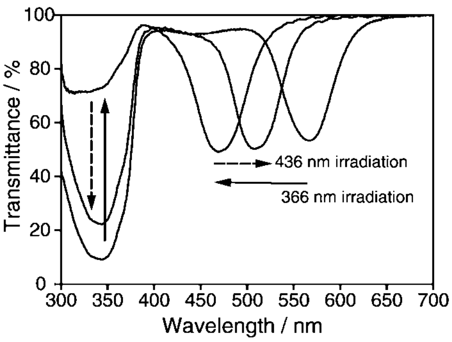


Fig. 6 The recovery of the reflection band in transmission spectra by the photoisomerization of **2d** from *Z* to *E* isomer. After irradiation of the cholesteric films with 366 nm light for 30 seconds at 92 °C, subsequent irradiation of the films with 436 nm light for 30 seconds was carried out.

shows $(\mathrm{d}P/\mathrm{d}T) < 0$.[3f] We also confirmed that the thermal and photo-isomerization from *Z* to *E* returned the pitch to its initial state. After the films were exposed to 366 nm light at the cholesteric temperature, subsequent irradiation with a 436 nm light, which caused the photoisomerization of the azobenzenes from the *Z* to *E* isomer, was carried out. As shown in Fig. 6, the shifted reflection band by the photoisomerization from the *E* to *Z* isomer returned to a longer wavelength due to the 436 nm irradiation.

On the other hand, the remarkable influence of the substituted alkyl chain on the cholesteric pitch was not observed for the *Z* isomers as observed for the *(E)*-azobenzenes (black and white squares in Fig. 3). All the *(Z)*-azobenzenes **2a–2h** would equally disorder the CLC phase. Therefore, the special interaction does not function in the systems of **1** and the *(Z)*-azobenzenes, with the result that *(Z)*-azobenzenes would merely behave as impurities in **1** and induce a slight shortening of the cholesteric pitch.

Isomerization of 4,4′-dialkylazobenzenes in the glassy solid state

After fixing the cholesteric molecular structure by rapid cooling, the *Z*–*E* thermal isomerization of the azobenzene derivatives embedded in it was observed. Fig. 7 shows the change in the transmission spectra of the glassy solid films at 22 °C after irradiation of the mixture consisting of 1 wt% of **2d** and **1** with 366 nm light at the cholesteric temperature (90 °C), and the spectrum of the solid film obtained without irradiation. The gradual recovery of the band around 340 nm in the spectra is attributed to the thermal isomerization of the azobenzenes from the *Z* to *E* form. This recovery was analyzed by the first-order plot of the equation

$$\ln\left(\frac{A_\infty - A_0}{A_\infty - A_t}\right) = kt$$

where A_t, A_0, and A_∞, are the absorbances at the peak of the π–π* band (340 nm) at times *t*, zero, and infinity, respectively. As shown in Fig. 8, the thermal *Z*→*E* isomerization of the azobenzene derivative in the cholesteric glassy solid exhibits deviation from first-order kinetics. Although the rate constant *k* is $4.4 \times 10^{-6}\ \mathrm{s}^{-1}$ in a benzene solution at 25 °C, as estimated from the slope of the dotted line in Fig. 8, *k* in the cholesteric glassy solid decreased with an increase in time. In some studies concerned with the thermal isomerization of azobenzenes in polymer matrices, an anomalous fast portion was observed in the early stage of the isomerization, which is due to the trapped azobenzenes with a strained confirmation.[13] However, our result did not include such a fast portion. Since the *Z* isomer was formed in the CLC phase with fluidity, and then confined in the rigid glassy solid by rapid cooling from the CLC phase, there would be no trapped *(Z)*-azobenzenes having a strained conformation though there was a difference in the free volume surrounding the *(Z)*-azobenzenes.

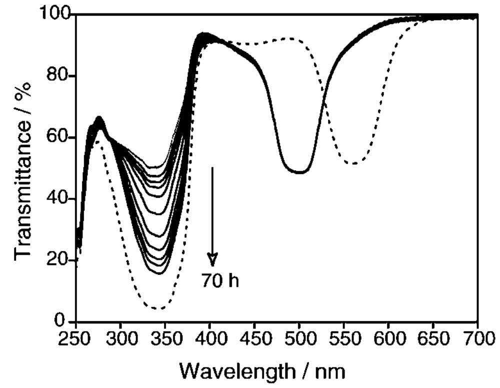


Fig. 7 Transmission spectrum of the super-cooled solid film obtained without irradiation (dotted line) and the change in the transmission spectra of the solid films obtained after irradiation while at 22 °C (solid lines). Solid films were prepared by dipping the mixture consisting of **1** and 1 wt% of **2d** between two glass plates into ice–water with or without irradiation with 366 nm light at 88 °C.

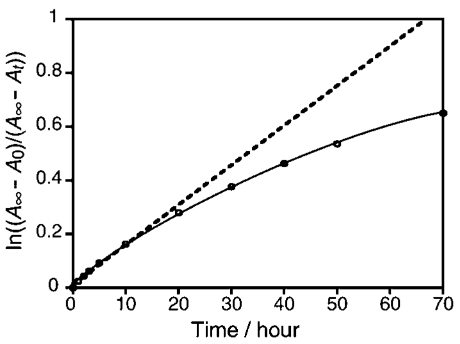
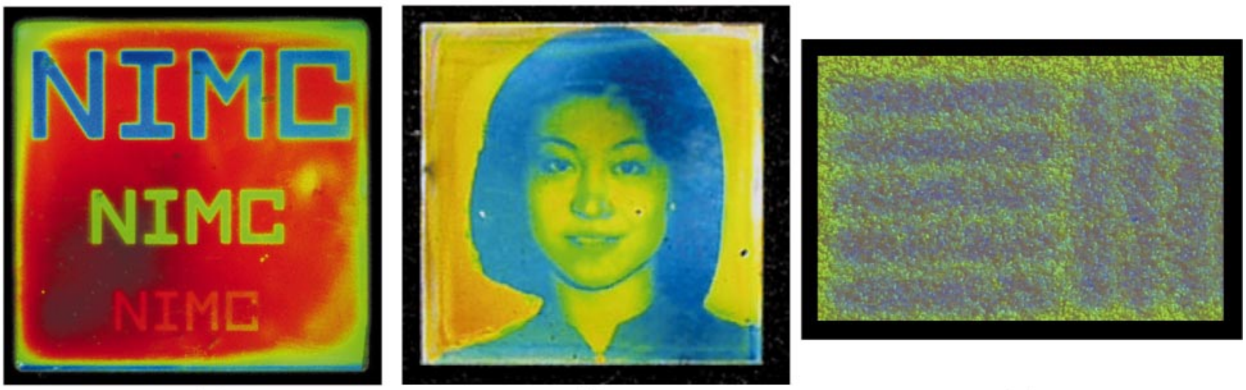


Fig. 8 First-order plot of the thermal *Z*→*E* isomerization of **2d** in the cholesteric glassy solid at 22 °C. Dotted line corresponds to the data for the *Z*→*E* isomerization of **2d** in benzene at 25 °C.

On the other hand, no change in the reflection band around 550 nm in Fig. 7 indicates that the fixed cholesteric structure is not perturbed by the thermal isomerization of the azobenzenes. Furthermore, neither the UV (366 nm) nor visible light (436 nm) from the high pressure Hg lamp, which caused the photoisomerization of the azobenzenes from *E* to *Z* and from *Z* to *E*, respectively, had any effect on the reflection bands of the solid films after rapid cooling. This result supports that the reflection change is not due to the change in refractive index induced by the isomerization of azobenzenes but due to the change in the helical pitch. If the reflection change is caused by the change in refractive index, the reflection should change even at the glassy solid state where the helical pitch is fixed. Regarding the stability of the fixed colour in the glassy solid state, although the glass transition temperature was lowered as the concentration of the azobenzenes increased, the reflected colour of the solid films containing 1 wt% **2d**, for example, was stable for at least one year at room temperature. Therefore it is noted that the cholesteric glassy solid of medium-molecular-weight CLC, containing photochromic azobenzenes, is an effective material for storage of the information written by a photon.

Repetitive recording of colour image using a combination of 4,4′-dialkylazobenzene and medium-molecular-weight CLC

The properties of the mixture of **1** and **2a–2h**, as described above, allow us to reversibly record colour images due to the cholesteric reflection in a photon mode. The reflection of our mixed systems covers all regions of visible light at the cholesteric temperature and the *E*–*Z* photoisomerization of



(a) (b) (c)

Fig. 9 Photographs of the super-cooled solid films of a mixture consisting of **1** and 2 wt% of **2d** between two glass plates. The mixture was exposed to 366 nm light through a mask at a certain temperature before cooling by dipping in an ice-bath. (a) The letter image of our institute name obtained by irradiation of the cholesteric films for 15 seconds at 87 °C. The mask used has a transmittance of 100, 25, 10% at the top, middle, and bottom of the "NIMC" characters, respectively, and 0% transmittance in areas other than the letters. As a result, "NIMC" characters showed blue, green, and orange colours in order from the top and the background was red. The sizes of the sides and the thickness of the glass plates are 20 mm and *ca.* 180 μm. (b) Photographic image of a lady prepared by irradiation of the cholesteric films for 15 seconds at 90 °C. (c) Microscopic observation of resolution pattern (25 μm) prepared by irradiation of the cholesteric films for 30 seconds at 93 °C.

the azobenzenes continuously shifts the reflection band. Hence, the colour can be selected by controlling the temperature, the concentration of the doped azobenzenes and extent of the photoisomerization. Fig. 9 shows images stored on solid films comprised of a mixture of **1** and **2d** (2 wt%). The images of our institute name with blue, green, and orange colours on a red background as shown in Fig. 9a were produced by the following procedure. A thin film in the red cholesteric phase was first obtained by keeping the mixture of **1** and **2d** between a set of glass plates on the hot stage at 87 °C after melting it above 120 °C. The thin film was irradiated with 366 nm light *via* the mask where each character transmitted the light with 100, 25, 10% in order from the top. At this stage, the character patterns with blue, green and orange colours were written on the film by the different energy of exposure which partially changed the extent of the photoisomerization, and the colour of the background, non-exposed area was maintained in red. Finally, the sample was transferred to an ice-bath for fixing the images. The reflection spectra of each part of this image are presented in Fig. 10. The image prepared from the mixture containing 1 wt% **2d** was maintained for at least a year at room temperature, although the stability of the image declined with an increase in the concentration of the azobenzenes. Upon re-heating the sample to isotropic temperature (above *ca.* 115 °C), the recorded image immediately disappeared and a new image could be recorded by exposing the sample through a new mask at the cholesteric temperature, because the isotropic temperature completely resets the molecular ordering of the CLC and the conformation of the azobenzene to the initial state (*E* form). This recording system can be used for photographic images as shown in Fig. 9b. Further, as seen in Fig. 9c, the resolution of the recorded image was at least 25 μm even when the cholesteric films were irradiated through one glass plate with *ca.* 150 μm thickness. Therefore, the recording of a full-colour image consisting of micrometre RGB dots will be possible for this recording system.

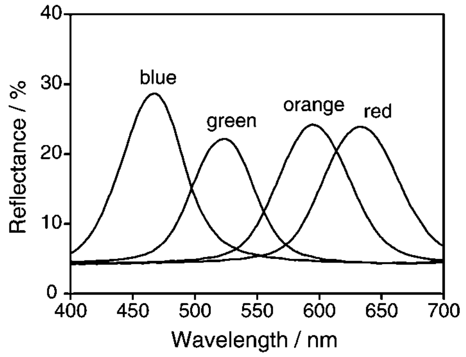


Fig. 10 Reflection spectra of each part of the images shown in Fig. 9a.

Conclusions

The effects of small amounts of achiral photochromic dopants, 4,4′-di-*n*-alkylazobenzenes **2a**–**2h**, on the helical pitch of the dicholesteryl ester **1** which formed a glassy solid that maintained the cholesteric structure after rapid cooling from the CLC phase, were investigated. Adding *(E)*-**2a**–**2h** to the host CLC **1** induced the pitch changes whose sense and extent were dependent on temperature, the concentration of the doped azobenzenes and the length of the substituted alkyl chain on the azobenzenes. In the case of doping the *(E)*-azobenzenes except for **2a** and **2h**, the pitch lengthened below 100 °C in comparison with the pitch of pure **1**. The lengthened pitch as a function of the alkyl chain length had a maximum value at $n = 11$ (90 °C). Consequently, it was revealed that reflected colour due to cholesteric pitch could be greatly expanded by the addition of achiral *(E)*-azobenzenes with appropriate length of substituted alkyl chain.

Upon irradiation, photoisomerization from *(E)*- to *(Z)*-**2a**–**2h** in the CLC phase always induced consecutive pitch shortenings in response to the formation of the *Z* isomers. Moreover, the pitches changed by the *E*–*Z* photoisomerization were always slightly shorter than the pitch of pure **1**, which was unrelated to the length of the substituted alkyl chain.

Since the mixed materials in this study had a property forming a glassy solid which maintained a cholesteric structure, the changed colour due to the changed pitch was fixed in the glassy solid. The fixed colour was not influenced by the isomerization of the azobenzenes any longer. Therefore, the colour was stably stored under general conditions. However, since the molecular arrangement of the CLC and the conformation of the doped azobenzenes completely returned to the initial state upon re-heating to isotropic temperature, the stored colour could be easily erased. From the fundamental investigations, it is revealed that mixed systems of **1** and small amounts of **2a**–**2h** enable one to write, store, and erase the optical image consisting of the cholesteric reflected colour, which can be utilised for a photo rewritable full-colour image recording.

Experimental

General methods

The mixtures of **1** and azobenzenes **2a–2h** were prepared by evaporation of dichloromethane from their mixed solutions. The CLC samples of the mixtures were prepared between two glass or quartz plates with temperature controlled by 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. Transmission and reflection spectra were recorded on UV-vis spectrophotometers (Shimadzu, UV-3100S and JEOL, MICRO-20 connected to UV-vis spectrophotometer). DSC measurements were performed on a Seiko Instrument SSC5200.

Materials

Dicholesteryl docosa-10,12-diynoate (**1**) was synthesised by a previously reported method.[7] 4,4′-Di-*n*-butylazobenzene (**2a**) and 4,4′-di-*n*-heptylazobenzene (**2b**) were synthesised by the oxidation of the corresponding anilines with manganese dioxide.[9,14] *p*-Butyl, heptyl, dodecyl, tetradecyl, and hexadecylanilines for preparation of the azobenzenes were obtained commercially. *p*-Undecyl, tridecyl, and pentadecylanilines were synthesised by the reactions of aniline and the corresponding *n*-alkyl alcohols such as undecan-1-ol with zinc chloride.[15]

4,4′-Di-*n*-undecylazobenzene (2c)

A mixture of *p*-undecylaniline (1.7 g) and activated manganese dioxide (3.0 g) in benzene (50 mL) was refluxed for 8 hours with azeotropic removal of the formed water. After the reaction mixture was cooled to room temperature, the manganese dioxide was filtered off and the filtrate solvent was removed *in vacuo*. The crude product was purified by chromatography on silica gel with dichloromethane as the eluent to give **2c** in 40% yield: $T_{\text{Cr-Sm}}$ 36 °C, $T_{\text{Sm-N}}$ 56 °C $T_{\text{N-I}}$ 60 °C. ^{1}H-NMR (CDCl$_3$, 270 MHz) δ 0.88 (t, 6H), 1.26–1.68 (m, 36H), 2.68 (t, 4H), 7.30 (d, 4H), 7.82 (d, 4H). Anal. Calcd for $C_{34}H_{54}N_2$: C, 83.20; H, 11.09; N, 5.71. Found: C, 83.41; H, 11.17; N, 5.71.

4,4′-Di-*n*-dodecylazobenzene (2d)

The synthetic procedure was the same as that for **2c** except *p*-dodecylaniline was used instead of *p*-undecylaniline. For **2d**: $T_{\text{Cr-Sm}}$ 51 °C, $T_{\text{Sm-I}}$ 60 °C. ^{1}H-NMR (CDCl$_3$, 270 MHz) δ 0.88 (t, 6H), 1.26–1.65 (m, 40H), 2.68 (t, 4H), 7.31 (d, 4H), 7.82 (d, 4H). Anal. Calcd for $C_{36}H_{58}N_2$: C, 83.33; H, 11.27; N, 5.40. Found: C, 83.50; H, 11.43; N, 5.33.

4,4′-Di-*n*-tridecylazobenzene (2e)

The synthetic procedure was the same as that for **2c** except *p*-tridecylaniline was used instead of *p*-undecylaniline. For **2e**: $T_{\text{Cr-Sm}}$ 51 °C, $T_{\text{Sm-I}}$ 65 °C. ^{1}H-NMR (CDCl$_3$, 270 MHz) δ 0.88 (t, 6H), 1.26–1.68 (m, 44H), 2.67 (t, 4H), 7.30 (d, 4H), 7.82 (d, 4H). Anal. Calcd for $C_{38}H_{62}N_2$: C, 83.45 ; H, 11.43 ; N, 5.12. Found: C, 83.57; H, 11.47; N, 5.03.

4,4′-Di-*n*-tetradecylazobenzene (2f)

The synthetic procedure was the same as that for **2c** except *p*-tetradecylaniline was used instead of *p*-undecylaniline. For **2f**: mp 62 °C. ^{1}H-NMR (CDCl$_3$, 270 MHz) δ 0.88 (t, 6H), 1.26–1.65 (m, 48H), 2.68 (t, 4H), 7.31 (d, 4H), 7.82 (d, 4H). Anal. Calcd for $C_{40}H_{66}N_2$: C, 83.56; H, 11.57; N, 4.87. Found: C, 83.71; H, 11.78; N, 4.57.

4,4′-Di-*n*-pentadecylazobenzene (2g)

The synthetic procedure was the same as that for **2c** except *p*-pentadecylaniline was used instead of *p*-undecylaniline. For **2g**: $T_{\text{Cr-Sm}}$ 60 °C, $T_{\text{Sm-I}}$ 69 °C. ^{1}H-NMR (CDCl$_3$, 270 MHz) δ 0.88 (t, 6H), 1.26–1.68 (m, 52H), 2.67 (t, 4H), 7.30 (d, 4H), 7.81 (d, 4H). Anal. Calcd for $C_{40}H_{66}N_2$: C, 83.65; H, 11.70; N, 4.65. Found: C, 83.90; H, 11.78; N, 4.56.

4,4′-Di-*n*-hexadecylazobenzene (2h)

The synthetic procedure was the same as that for **2c** except *p*-hexadecylaniline was used instead of *p*-undecylaniline. For **2h**: mp 70 °C. ^{1}H-NMR (CDCl$_3$, 270 MHz) δ 0.88 (t, 6H), 1.21–1.65 (m, 56H), 2.68 (t, 4H), 7.31(d, 4H), 7.82 (d, 4H). Anal. Calcd for $C_{44}H_{74}N_2$: C, 83.74; H, 11.82; N, 4.44. Found: C, 83.59; H, 11.98; N, 4.34.

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