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Reversible alignment change of liquid crystals induced by photochromic molecular films

XVIII. α-Hydrazono-β-keto esters as command molecules [1]

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The nematic director alignment in the liquid crystal cell was reversibly regulated by the geometrical isomerization of α-hydrazono-β-keto esters chemically linked on the substrate surface. Two methods for the surface modification were employed successfully. Method I was based on direct modification of substrates with α-hydrazono-β-keto ester units having a silylating group. Cells fabricated with these substrates showed altering reversible liquid crystal alignment through a combination of photoirradiation and heating. In method II, ω-acryloyloxyalkyl α-hydrazono-β-keto ester units were introduced through Michael addition to substrates modified with 3-aminopropyltriethoxysilane. The liquid crystal alignment in this case altered reversibly according to the reversible photoisomerization of the α-hydrazono-β-keto units on the substrates. The results strongly support the observation that a change in molecular shape, due to geometrical isomerization, is responsible for regulating the nematic director alignment.

1. Introduction

Alignment of liquid crystals between vertical (homeotropic) and parallel modes in the nematic mesophase is regulated by geometrical photoisomerization of monolayered azobenzenes bound on substrate surfaces [2]. This phenomenon offers the possibility of constructing photoresponsive liquid crystal cells with potential application for photomemory and display devices [3]. Photoactive surfaces which regulate liquid crystal alignment have been named ‘command surfaces’ since a single azobenzene molecular unit can control the alignment alteration of *c.* 10^4 liquid crystal molecules during the process of photoisomerization [2]. Systematic studies have revealed several factors determining photo-induced alignment control at the molecular level. The substitution of a hydrophobic alkyl residue as a head group at the

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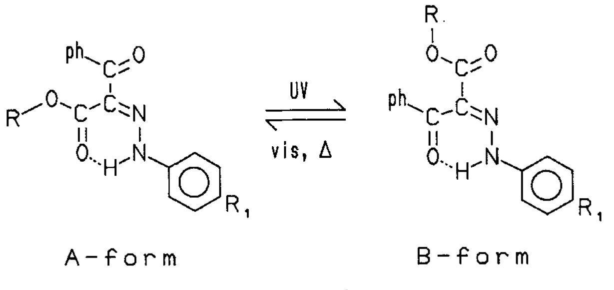
azobenzene moiety [4] or comodification with a long alkyl chain under controlled reaction conditions [5] effectively controls the alignment alteration between the homeotropic and planar modes through photoisomerization of the azobenzene unit. Further, the occupied area per azobenzene unit on substrate surfaces should be less than about 100 Å^2 for effective performance [4].

The photocontrol of liquid crystal alignment has been proposed as follows. The *trans*-isomer units with rod-like molecular shape cause the surrounding liquid crystal molecules to become almost vertical with respect to the substrate surface. Upon exposure to UV light, deformation of the molecular shape of the photochromic unit takes place, such that reorientation of the liquid crystal molecules surrounding the azobenzene units is induced. The bent form of the *cis*-isomer may be favourable for the parallel alignment of the nearest neighbour liquid crystal molecules. Successive reorientation occurs throughout the cell resulting in the parallel alignment of all liquid crystal molecules lying over the irradiated area. This interpretation has been supported by the fact that a stilbene unit attached on a glass surface acts as a command molecule [6]; the photoisomerization of stilbene is accompanied by the remarkable change in shape between the rod-like and the V-shaped molecules in a manner quite similar to that of azobenzenes.

The extension of the command surfaces to other photochromic molecular layers is of significance, not only for obtaining a further clue to help elucidate the mechanism of the alignment photocontrol, but also from a practical point of view. This paper deals with the regulation of liquid crystal alignment by α-hydrazono-β-keto esters (HKEs) which exhibit similar changes in molecular shape during photoisomerization to those of azobenzenes and stilbenes. According to Courtot and coworkers [7], isomerization in solutions results in switching the hydrogen bonding of the hydrazono hydrogen atom (see Scheme 1). Upon exposure to UV light, the hydrogen bond acceptor switches from the oxygen atom of the ester carbonyl (A-form) to the oxygen atom of the acyl carbonyl (B-form). The reverse process occurs upon either heating or exposure to visible light. The hydrogen bonding causes the molecules of both isomers to be sufficiently rigid, such that they hold their molecular shapes in the stable condition.



Scheme 1.

2. Experimental

2.1. *Materials*

2-Arylhydrazono-3-oxo-3-phenylpropionate. The preparative procedure for 2-(4-hexylphenylhydrazono)-3-oxo-3-phenylpropionic acid (**1a**) is given as a typical example. Hexylaniline (7·2 g) was added dropwise to 20 ml of concentrated HCl containing a small amount of an emulsifier, Liponox NA, and 10 ml of cold water. A solution of 3·2 g sodium nitrite in 20 ml of water was added to the emulsion below 10°C and stirred for 30 min (below 10°C) to give a clear diazotized solution which was neutralized with sodium acetate and sodium carbonate solutions. The diazotized solution was added dropwise below 10°C to a solution of 5·0 g of sodium acetate and 7·7 g of ethyl benzoylacetate in a mixture of 20 ml of water and 30 ml of methanol. While stirring for 30 min at this temperature, the yellow solution turned orange. After further stirring for 2 h at room temperature, red oily products were extracted with methylene chloride. The extracts were dried over sodium sulphate, and removal of the solvent gave 14 g of crude ethyl 2-arylhydrazono-3-oxo-3-phenylpropionate as a red oil which was added to a solution of ethanol (60 g) and 2·2 g of potassium hydroxide and heated under reflux for 1 h to give a clear solution. The potassium salt of 2-arylhydrazono-3-oxo-3-phenylpropionic acid deposited upon cooling and was collected by filtration, washed with methanol and dried: yield 7·2 g (45 per cent), mp 134–136°C. The potassium salt (1·2 g) was stirred in 2 mol of concentrated HCl in 20 ml water at 40–50°C for 1 h. Insoluble crystals were collected and recrystallized from methanol to give 0·6 g of needles of the free acid of mp 94°C and *m/e* of 353 (Mw 352). δ_H($CDCl_3$), 0·85 (3 H, t, CH_3), 1·3–1·65 (8 H, m, $(CH_2)_4Me$), 2·65 (2 H, t, $ArCH_2$), 4·45 (1 H, s, NH), 7·25–7·86 ppm (9 H, m, ArH).

Potassium 2-(4-methoxyphenylhydrazono)-3-oxo-3-phenylpropionate and the corresponding acid of mp 155–157°C were prepared in a similar manner.

ω-Carboxyalkyl 2-arylhydrazono-3-oxo-3-phenylpropionate. The preparation of carboxymethyl 2-(4-hexylphenylhydrazono)-3-oxo-phenylpropionate (**1b**) is given as a typical example. A mixture of 1 g of the potassium salt and 0·55 g of *tert*-butyl bromoacetate in 10 ml of DMF was stirred for 1 h at 40°C. After the solution was treated with water, the products were extracted with benzene. The combined benzene extracts were washed with aqueous sodium chloride, dried over sodium sulphate and evaporated to dryness. The residual solid was dissolved in ethanol and the solution, to which was added 1 ml of concentrated HCl, was stirred for 1 h at room temperature. After the solvent was evaporated under diminished pressure, the residue was dissolved in methylene chloride, washed with water and dried. Removal of the solvent gave a yellow solid which was recrystallized from methanol to afford 0·5 g of yellow needles of mp 123–124°C and *m/e* of 410 (MW 410). δ_H($CDCl_3$), 0·85 (3 H, t, CH_3), 1·3–1·6 (8 H, m, $(CH_2)_4Me$), 2·57 (2 H, t, $ArCH_2$), 4·6 (1 H, s, NH), 4·77 (2 H, s, OCH_2CO), 7·1–7·95 ppm (9 H, m, ArH).

Carboxymethyl 2-(4-methoxyphenylhydrazono)-3-oxo-3-phenylpropionate (**1d**) of mp 137–138°C and *m/e* of 356 (MW 356) was prepared in a similar fashion. δ_H($CDCl_3$), 3·75 (3 H, t, OCH_3), 4·62 (1 H, s, NH), 4·74 (2 H, s, OCH_2CO), 6·82–7·88 ppm (9 H, m, ArH). 5-Carboxypentyl 2-(4-hexylphenylhydrazono)-3-oxo-3-phenylpropionate (**1c**) of mp 45–52°C and *m/e* of 467 (MW 467) was synthesized similarly using 6-bromohexanoic acid instead of *tert*-butyl bromoacetate. δ_H($CDCl_3$), 0·87 (3 H, t, CH_3), 1·3–1·6 (8 H, m, $(CH_2)_4Me$), 1·45–1·75 (6 H, m, $(CH_2)_3$), 2·37 (2 H, t, CH_2CO), 2·58 (2 H, t, $ArCH_2$), 4·1 (1 H, s, NH), 4·3 (2 H, s, OCH_2), 7·12–7·98 ppm (9 H, m, ArH).

ω-Acryloyloxyalkyl 2-arylhydrazono-3-oxo-3-phenylpropionate. The preparative procedure for 2-acryloyloxyethyl 2-(4-hexylphenylhydrazono)-3-oxo-3-phenylpropionate (**3a**) is given as a typical example: A mixture of 1·00 g of potassium 2-(4-hexylphenylhydrazono)-3-oxo-3-phenylpropionate and 0·38 g of 2-bromoethanol in 10 ml of DMF was stirred at 60°C for 4 h and mixed with water and benzene to extract the product. The benzene layer was washed with aqueous sodium chloride solution, dried over sodium sulphate and evaporated to dryness to yield an oily residue. The oil was dissolved in dry ether, and 0·25 g of acryloyl chloride was added to the solution at

10–15°C and stirred for 1 h. To the reaction mixture was added 0·25 g of triethylamine. After stirring for 3 h and evaporating these ether, methylene chloride and water were added to the mixture. The organic layer was washed with aqueous sodium carbonate solution and subsequently with water and dried over sodium sulphate. Evaporating the solvent gave a yellow oil which was purified by silica gel column chromatography using a 2 : 1 mixture of benzene and ethyl acetate as eluent to afford 0·48 g of a viscous yellow oil of *m/e* 450 (MW 450). $\delta_H(CDCl_3)$, 0·88 (3 H, t, CH_3), 1·3–1·65 (8 H, m, $(CH_2)_4$), 2·57 (2 H, t, $ArCH_2$), 4·25 (1 H, s, NH), 4·48–4·62 (4 H, m, $O(CH_2)_2O$), 5·85 and 6·45 (1 H, d, COC=CH), 6·15 (1 H, t, COCH=C), 7·13–8·1 ppm (9 H, m, ArH).

In a similar way, we synthesized 6-acryloyloxyhexyl 2-(4-hexylphenylhydrazono)-3-oxo-3-phenylpropionate (**3b**, $\delta_H(CDCl_3)$, 0·87 (3 H, t, CH_3), 1·3–1·72 (16 H, m, CH_2), 2·57 (2 H, t, $ArCH_2$), 4·15 and 4·3 (2 H, t, OCH_2), 5·83 and 6·42 (1 H, d, COC=CH), 6·13 (1 H, t, COCH=C), 7·12–7·92 ppm (9 H, m, ArH)), 11-acryloyloxyundecyl 2-(4-hexylphenylhydrazono)-3-oxo-3-phenylpropionate (**3c**, *m/e* 576, MW 576, $\delta_H(CDCl_3)$, 0·88 (3 H, t, CH_3), 1·3–1·7 (26 H, m, CH_2), 2·57 (2 H, t, $ArCH_2$), 4·15 and 4·3 (2 H, t, CH_2O), 5·82 and 6·35 (1 H, d, COC=CH), 6·15 (1 H, t, COCH=C), 7·13–7·92 (9 H, m, ArH)) and 6-acryloyloxyhexyl 2-(4-methoxyphenylhydrazono)-3-oxo-3-phenylpropionate (**3d**, *m/e* 452, MW 452, $\delta_H(CDCl_3)$, 1·45–1·75 (8 H, m, CH_2), 3·8 (3 H, s, OCH_3), 4·17 (2 H, t, OCH_2), 4·32 (2 H, t, CH_2O), 5·83 (1 H, d, COC=CH), 6·13 (1 H, t, COCH=C), 6·42 (1 H, d, COC=CH), 6·87–7·92 ppm (9 H, m, ArH)). They were all oily substances.

2.2. *Spectroscopic measurements*

The chemical structure of the compounds obtained was confirmed by NMR (JEOL-JNM-GSX270) and IR (JASCO J-0068) spectroscopies. The electronic absorption spectra were measured by using a photodiode array spectrophotometer (HP8452A).

2.3. *Substrate surface modification*

Method I. α-Hydrazono-β-keto acid (**1a**) and ω-carboxyalkyl HKEs (**1b–d**) were condensed with an equimolar amount of 3-aminopropyltriethoxysilane in methylene chloride by means of dicyclohexylcarbodiimide for 4 h at room temperature. After removal of dicyclohexylurea and the solvent, the silylating compounds obtained were dissolved in ethanol to prepare 1 wt% solutions. Cleaned quartz plates were treated with this ethanolic solution to obtain the surface modification in similar ways to that described in our previous paper [4].

Method II. Cleaned quartz plates were boiled in 1 wt% solutions of 3-aminopropyltriethoxysilane in toluene for 10 h, twofold supersonication in chloroform for 10 min, followed by drying at 120°C for 30 min. The plates were dipped in a 0·5–1·0 wt% ethanolic solution of ω-acryloyloxyalkyl HKEs (**3a–d**) for 30 min, and air-dried plates were heated at 120°C for 1 h and cleaned by supersonication in benzene for 5 min. The plates were air-dried after rinsing with ethanol.

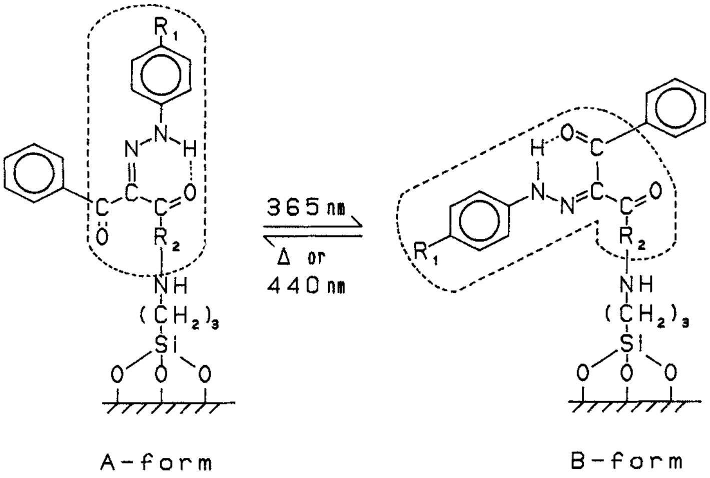
2.4. *Cell construction and photoresponse measurements*

A cell filled with a cyclohexanecarboxylate-type nematic liquid crystal (DON-103; K–17–N–73–I, Rodic Co.) and suspending 8 μm rod glass spacers was fabricated according to our paper [4]. The photoirradiation was carried out by using a 500 W high pressure mercury lamp through a combination of Corning filters (7–51 and 0–52) for the 365 nm light (*c.* 10 mW cm^{-2}) and through filters (5–57 and 3–73) for the visible light (*c.* 5 mW cm^{-2}). The photoresponse of the liquid crystal cells was monitored by the transmittance of a polarized He–Ne laser through a crossed polarizer.

3. Results and discussion

3.1. *The photochromism of HKEs in solution and on quartz plates*

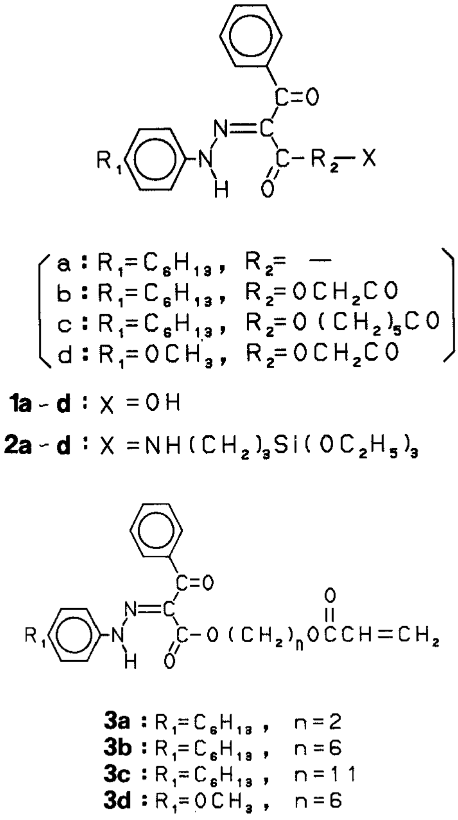
The photochromism of HKE involving reversible structural alteration between the rod-like and V-shaped molecular forms has attracted our interest since the analogous isomerization of azobenzene proves powerful for regulating the liquid crystal alignment change between the homeotropic and parallel modes [2]. Our studies on the azobenzene monolayer as the command surface have revealed that a substituted group at the head portion of the chromophore plays an important role in the liquid crystal alignment alteration [4]. Therefore, we introduced a hexyl or methoxy group as a head substituent at the phenyl ring of the hydrazono group of HKE, and used the triethoxysilyl group as an alkyl ester residue to attach the photochromic unit to the silica surface. As seen in scheme 2, the introduction of substituents in this way causes its HKE to change molecular shape similar to that of azobenzenes substituted at *para* positions.



Scheme 2

Two methods of surface modification were employed successfully. One of these (method I) was based on direct introduction of the HKE unit through siloxy bond formation [4]. For this purpose, we synthesized one α-hydrazono-β-keto acid (**1a**) and three ω-carboxyalkyl HKEs (**1b–d**), which were condensed with 3-aminopropyltriethoxysilane to afford the silylating reagents (**2a–d**) as shown in scheme 3. The other method (method II) is the Michael addition reaction [8] of the ω-acryloyloxyalkyl HKEs (**3a–d**) with amino groups on quartz plates which were treated with 3-aminopropyltriethoxysilane in advance. The HKE derivatives used in both methods have varying lengths of alkyl chain spacer since the spacer length attaching the azobenzene moiety to the silica surface affects the command efficiency crucially.

The photochromism of all the HKEs synthesized in this study was confirmed in dichloromethane. The examples are illustrated in figure 1. The A-form of almost all derivatives has an absorption maximum at *c.* 370 nm except for **1d** and **3d** showing a red shift of *c.* 10 nm, which have a methoxy substituent at the phenyl ring. The exposure of solutions to 365 nm light resulted in the appearance of new absorption bands around 410 nm for **1d** and **3d** and around 400 nm for the other compounds due to the formation of the B-form, accompanied by isosbestic points. Irradiation of the solutions with light



a : $R_1=C_6H_{13}$, $R_2=$ —
b : $R_1=C_6H_{13}$, $R_2=OCH_2CO$
c : $R_1=C_6H_{13}$, $R_2=O(CH_2)_5CO$
d : $R_1=OCH_3$, $R_2=OCH_2CO$

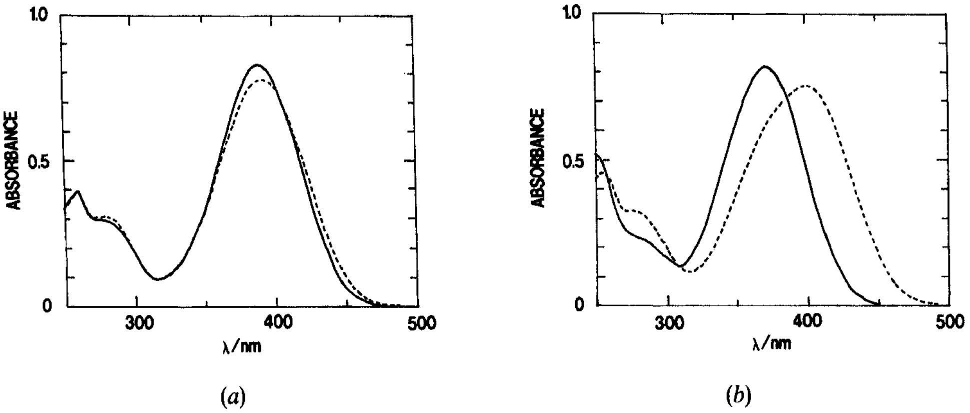
1a-d : $X=OH$
2a-d : $X=NH(CH_2)_3Si(OC_2H_5)_3$

3a : $R_1=C_6H_{13}$, $n=2$
3b : $R_1=C_6H_{13}$, $n=6$
3c : $R_1=C_6H_{13}$, $n=11$
3d : $R_1=OCH_3$, $n=6$

Scheme 3

of wavelength longer than 440 nm caused the reverse isomerization to recover the absorption ascribable to the A-form.

Photochromism in solutions was influenced considerably by the nature of the solvent. While quantitative formation of the B-form was observed in the photostationary state upon exposure to 365 nm light in dichloromethane, the A-form remained unchanged considerably in acetonitrile. Since the absorption spectra in both solvents were quite similar in general form and peak positions, the photostationary yields of the



(*a*) (*b*)

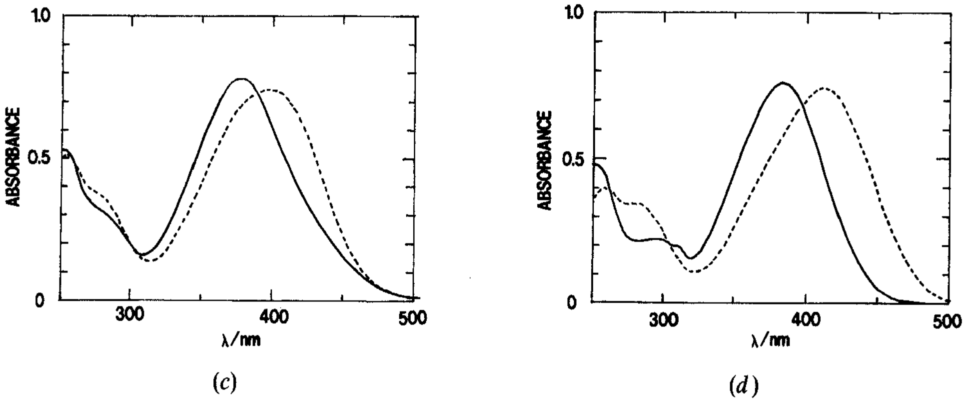


Figure 1. Absorption spectra in dichloromethane after irradiation with 365 nm light (dashed line) and 440 nm light (solid line): (*a*) **1a**, (*b*) **1b**, (*c*) **1c**, and (*d*) **1d**.

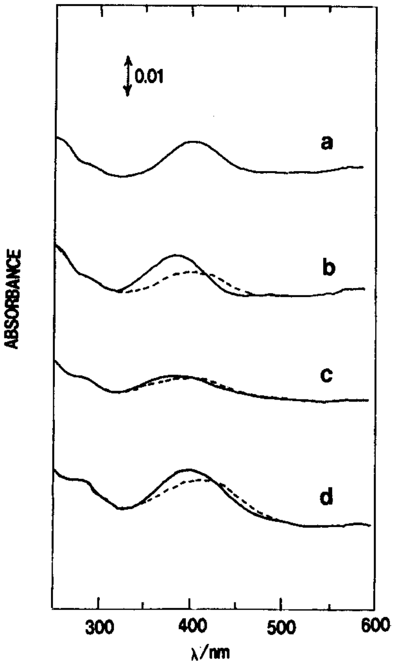


Figure 2. Absorption spectra of quartz plates modified with **2a** (*a*), **2b** (*b*), **2c** (*c*), and **2d** (*d*) before (solid line) and after (dashed line) irradiation with 365 nm light.

B-form depend on the thermal stability of this form in these solvents. Indeed, the thermally induced reverse reaction from the B-form to the A-form took place much slower in dichloromethane that in acetonitrile. In such a protic solvent as methanol, no photoisomerization was observed upon exposure to the light, indicating that the B-form is thermodynamically unstable because of the interruption of the intramolecular hydrogen bonding by the solvent molecules.

Figure 2 shows the electronic absorption spectra of quartz plates modified with HKE monolayer according to method I, before and after irradiation with 365 nm light. The photoisomerization from the A-form to the B-form was confirmed for plates modified with **2b**, **2c** and **2d** whereas no spectral change was obtained for a plate modified with **2a**. This may reflect the spacer length effect and/or the transformation of hydrogen bonding acceptor ability from the ester carbonyl to the amide carbonyl. In marked contrast to solution photochromism, HKE units attached on quartz surface exhibited no reverse isomerization from the B-form to the A-form upon exposure to visible light. Moreover, the B-form was so stable that no thermal isomerization took place, even if the plates (P-**2b**, P-**2c** and P-**2d**) were heated above 100°C.

On the other hand, HKE units attached on quartz surfaces by method II showed reversible photochromism. Very interestingly and in strong constrast to the results for method I, the reverse isomerization from the B-form to the A-form was found to proceed smoothly upon exposure to visible light. Needless to say that the heat treatment of plates covered with the B-form also resulted in the recovery of the A-form. The anomalous stability of the B-form attached to the silica surface by method I is thus ascribable to the nature of the molecular structure of the spacer unit in the silylating agent (**2**). The comparison of the spacer length in method I with that in method II reminds us of the spacer length effect; a longer spacer seems favourable to photo-induced reversible isomerization. An alternative characteristic of the spacer in method II is the larger flexibility of the spacer chain which incorporates a secondary amino group. Thus, the free movement of HKE units prepared by method II seems to be enhanced by longer as well as more flexible spacer chains. In other words the molecular motion of the B-form of the HKE unit in method I may be suppressed by the relatively rigid spacer chain. Further studies will be required to elucidate the stabilization mechanism of the B-form in method I.

3.2. *Alignment regulation*

In the table are summarized the liquid crystal alignment modes of nematic liquid crystal cells fabricated with surface-modified quartz plates before and after exposure to UV light. The initial mode was homeotropic for all cells consisting of plates prepared by method I. The cells allowed no transmittance when placed between a couple of crossed polarizers. Exposure to UV caused the cells to become bright, except for the liquid crystal cell fabricated with plates modified with **2a** (P-**2a**). The inactiveness of this cell is obviously ascribable to the absence of the photochromic reaction of the α-arlhydrazonobenzoylacetamide moiety.

Figure 3 shows the transmittance change of a linearly polarized He–Ne laser beam passed through liquid crystal cells fabricated with P-**2b**, P-**2c** and P-**2d** plates, respectively, and a crossed polarizer. The increase in the transmittance of the monitoring laser beam upon UV exposure is a result of the liquid crystal molecules being transformed into parallel alignment. The transmittance of the UV-exposed cells was not altered even on prolonged standing at room temperature, indicating that photoimages are markedly stable. Furthermore, no change in the transmittance of the

Electronic absorption spectra of quartz plates modified with HKE units and the liquid crystal alignment modes of cells made from them.

				Alignment modes§			
					Exposure to		
Plate	Modifier	Method†	λ_{max} nm‡	Initial	UV	Vis	Heating¶
P-**2a**	**2a**	I	400	h	h	h	—
P-**2b**	**2b**	I	380	h	p	p	h
P-**2c**	**2c**	I	380	h	p	p	h
P-**2d**	**2d**	I	395	h	p	p	h
P-**3a**	**3a**	II	370	h	p	h	h
P-**3b**	**3b**	II	370	h	p	h	h
P-**3c**	**3c**	II	370	h	p	h	h
P-**3d**	**3d**	II	380	r	r	r	—

† See text.
‡ Absorption maximum wavelength of the A-form.
§ h: homeotropic, p: planar, r: random.
¶ 65–70°C.

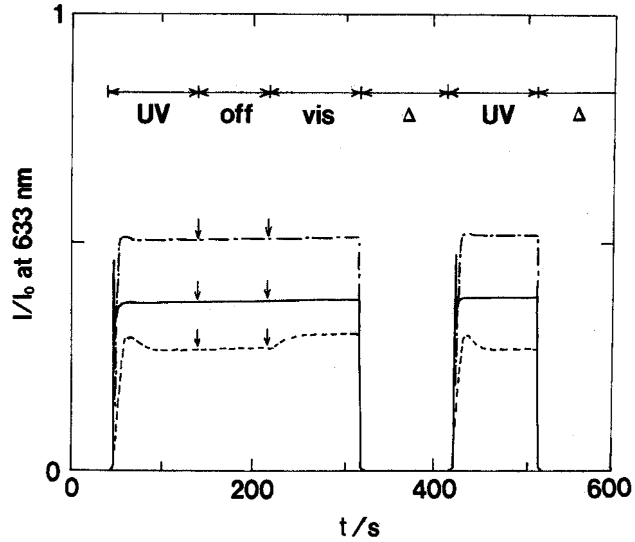


Figure 3. The photoirradiation and heating responses of nematic liquid crystal cells consisting of substrates chemically modified with **2b** (solid line), **2c** (dashed line), and **2d** (broken line) monitored with the transmittance of a linearly polarized He–Ne beam through a crossed polarizer.

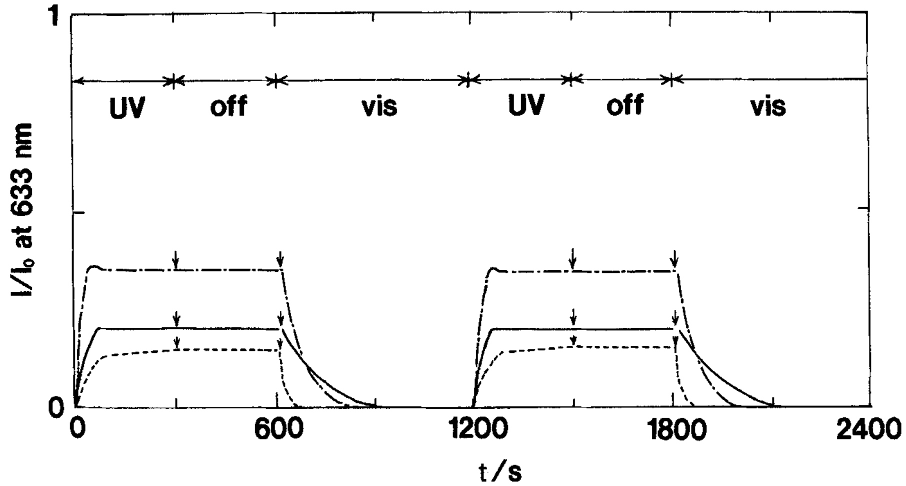


Figure 4. The photoresponses of nematic liquid crystal cells consisting of substrates chemically modified with **3a** (solid line), **3b** (broken line), and **3c** (dashed line) monitored with the transmittance of a linearly polarized He–Ne beam through a crossed polarizer.

monitoring He–Ne beam was induced upon exposure to visible light, since the B-form was extraordinarily stabilized on the substrate surface. The recovery of the initial homeotropic alignment was achieved only by heating the cell at 65–70°C. Thus, the repetitive response of liquid crystal cells modified with HKE units by method I can be achieved by applying a combination of UV light and heat energy. The anomalous response behaviour of the cells is unequivocally due to the stabilization of the B-form of the HKE unit in the monolayer bound to the silica surface. This is of potential value for obtaining a photomemory stable to ambient light and temperature.

The photoresponse of cells fabricated with plates prepared by method II is also compiled in the table. The behaviour of these cells was in striking contrast to that of the cells made from plates modified by method I. Firstly, photoisomerization in the former cells demonstrated reversible response upon alternate exposure to UV and visible lights, as clearly shown in figure 4. Secondly, planar alignment of UV-exposed cells prepared according to method II reverses to homeotropic alignment gradually on standing at room temperature in the dark whereas no reverse process took place when cells were constructed with plates modified by method I. Thirdly, a methoxy substituent at the phenyl ring showed different effects on the liquid crystal alignment mode as well as on the photoresponse. A liquid crystal cell consisting of P-**2d** prepared by method I was a photoresponsive cell, whereas a cell consisting of P-**3d** prepared by method II maintained random parallel alignment irrespective of the isomerization of the HKE unit. The latter case has a marked resemblance to a cell fabricated with plates modified with a *p*-methoxyazobenzene monolayer [4]. Further studies on the relationship between molecular structure and function should be required to elucidate the unusual ability of **1d**.

In conclusion, HKE units are able to regulate the reorientation of liquid crystal molecules, strongly supporting the ability to change molecular shape due to geometrical isomerization is one of the requirements for command molecules. We should stress here that HKE photochromism may have less practical significance by itself in a conventional sense because the absorption maxima of both forms are not well-separated. Indeed, as seen in figure 2, the spectral alteration of HKE attached to a silica surface is quite minute with respect to both shifts in λ_{max} and absorbance. However, such a negligibly small spectral change is dramatically amplified with liquid crystal alignment alteration to help visualize photoimages to the naked eye.

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