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Command surfaces 12 [1]. Factors affecting in-plane photoregulation of liquid crystal alignment by surface azobenzenes on a silica substrate

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Command surfaces 12 [1]. Factors affecting in-plane photoregulation of liquid crystal alignment by surface azobenzenes on a silica substrate

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In-plane alignment of nematic liquid crystals was regulated by polarized-light-irradiation of a cell assembled with a silica plate, the surface of which was modified by attaching 4-hexyl-4′-hexyloxyazobenzene at its *o*-position through surface silylation. The photoisomerizability of the chemisorbed azo-chromophore was affected by their surface density and the nature of photoinactive co-modifiers. The efficiency of the photoregulation of liquid crystal alignment was optimized by two-dimensional dilution of the chromophore with ethyltriethoxysilane (ETS) or 3-aminopropyltriethoxysilane (ATS). As a result, favourable procedure was to modify a silica surface with a crude azo-silylating reagent contaminated by ATS. The rate of the photoinduced reorientation of liquid crystals was followed by monitoring the alteration of the alignment direction of a dichroic dye dissolving in a mesophasic layer upon exposure to linearly polarized light. Exposure energy for the in-plane reorientation of a liquid crystal was about 100 mJ cm^{-2} of 445 nm light at elevated temperatures close to T_{NI}. The effect of positional isomerism on the photoregulation was determined with the use of 4-cyano-4′-hexyloxyazobenzene as a commander molecule. It was confirmed that the photoalignment efficiency was markedly enhanced by attaching the chromophore at the *ortho*- or *meta*-position. The exposure energy for the reorientation of a liquid crystal was reduced by linking the *p*-cyanoazobenzene at the *meta*-position so that the reorientation was complete with an exposure energy of 20 mJ cm^{-2}.

1. Introduction

Photochemically induced switching of liquid crystal (LC) alignment has been attracting current interest in relation to potential applicability to optical as well as display devices [2]. Surface-assisted alignment photoregulation using the 'command surface' effect provides an effective way to light-driven optical elements exhibiting reversibility [2, 3(*b*)]. The first example of this type of LC photoregulation was a reversible out-of-plane alignment alteration between homeotropic (perpendicular) and planar (parallel) modes using molecular layers of an azobenzene upon alternate irradiation with UV and visible light for the reversible photoisomerization [4]. In these systems, the term 'photochromic' sounds rather inappropriate since photoinduced structural change of monolayered molecules displayed no essential colour change to the naked eye. In this respect, photoactive surface molecules should be called 'commander molecules' in order to emphasize their decisive role in the alignment control of LC as 'soldier molecules'. As an extension of our work on this type of the alignment photocontrol based on the commander/soldier concept, we reported that azimuthal (in-plane) reorientation of LC molecules is induced by exposing an LC cell to linearly polarized UV light for the *E*/*Z* photoisomerization [5] and linearly polarized visible light for the *Z*/*E* photoisomerization [6, 7]. Closely related phenomenon induced by polarized light was found independently by Gibbons *et al.*, who employed a polyimide doped with a dichroic dye for a photoactive layer [8]. This photochemical procedure to result in a homogeneous alignment by linearly polarized light is of practical significance not only to apply to reversible as well as irreversible optical elements [9], but also to produce

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LC aligning layers applicable to conventional LC display devices [10]; a homogeneous alignment has been performed by a photolithographic technique without any troublesome rubbing treatment [11].

Substrate surfaces active to linearly polarized light irradiation have been so far modified according to the following methods to give command surfaces. One of these consists of surface modification of a silica plate with silylating reagents having a photochromic unit like azobenzene [6, 7] and spiropyran [12] which are linked covalently to topmost surfaces. Surface-selective modification of a poly(vinyl alcohol) thin film covering a substrate plate with azobenzenes as the second method is also effective for the alignment photoregulation [13]. The third method is based on covering a substrate plate with a thin film of polymers substituted with azobenzenes. Spin-coating [14, 15] and Langmuir–Blodgett deposition [16] are both relevant techniques. Spin-coating of a polymer doped with low-mass dye molecules on a substrate plate has been also used [8, 9, 17]. Closely related LC alignment regulation by polarized photochemistry has been performed by spin-coating a thin film of conventional photoresists, poly(vinyl cinnamates), which are crosslinked by the (2 + 2) cycloaddition [10, 18].

We have proposed recently the concept of molecular rotors which consist of a rod-like azobenzene skeleton linked to a silica surface through a polymethylene spacer as a molecular axle and rotates by the action of linearly polarized light to lead to the reorientation of LC molecules [6]. The main concern of this paper is to reveal the structure/functional relationship of this type of azobenzenes as commander molecules on silica plates. The surface silylation of a silica plate was employed here on account of the following. First, surface-specific modification with commander molecules are readily realized because binding sites of silanols are localized exclusively on an uppermost silica surface [19]. This situation gives us direct information concerning the participation of monolayered commander molecules in the alignment regulation by observation of aligned textures. Second, a tightly networked silica matrix eliminates completely the possibility that organic residues on a surface migrate into the inside of a substrate surface layer. This type of mobility of surface has been frequently observed in polymeric systems [20]. Thirdly, the highly crosslinked network of silica prohibits thoroughly the penetration of LC molecules into matrix [14] to give persistent alignment. Therefore, this system seems to be more adequate to elucidate the photoinduced reorientation mechanism because it is not necessary to take the role of a polymer backbone into account.

2. Experimental

2.1. *Materials*

2-Hydroxy-4-hexyloxy-4′-hexylazobenzene [6(*b*)], 2-(5-carboxyundecyloxy)-4-hexyloxy-4′-hexylazobenzene [6(*b*)] and 6-[4-(4-cyanophenyl)azo]phenoxy) hexanoic acid were prepared according to our previous papers [7]. Nematic liquid crystals (see figure 1), DON-103 (**1**) of $T_{NI} = 74°C$ and EXP-CIL (**2**) of $T_{NI} = 31·5°C$, were kindly donated by Rodic Co., Ltd. A dichroic dye (**3**) was donated by Nippon Kayaku Co., Ltd.

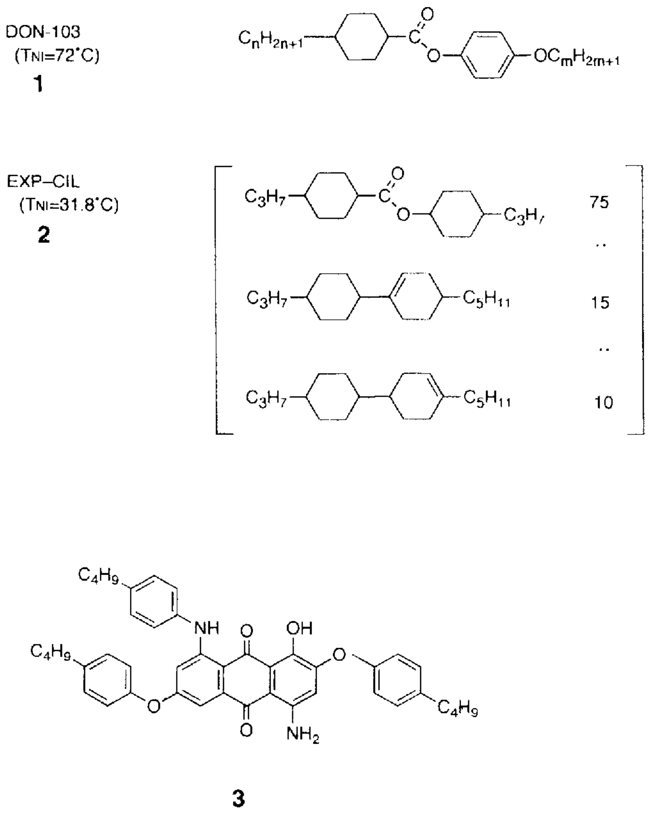

Figure 1. Chemical structures of liquid crystals and a dichroic dye.

2.1.1. *2-Carboxymethoxy-4-hexyloxy-4′-hexylazobenzene*

A mixture of 1·0 g 2-hydroxy-4-hexyloxy-4′-hexylazobenzene, 0·5 g ethyl bromoacetate and 0·5 g potassium carbonate in 10 ml DMF was stirred at 60°C for 4 h. After removing insoluble materials and adding hexane, the solution was washed with water. The organic layer was dried over anhydrous sodium sulphate and evaporated to dryness to give a crystalline residue which was recrystallized from ethanol. 1 g of potassium hydroxide was added to an ethanolic solution of the crystals, and the mixture was stirred at 50°C for 2 h, followed by acidification with hydrochloric acid and extracting with a mixture of ethyl acetate and hexane. The solution was washed with water and dried over anhydrous magnesium sulphate, followed by evaporation to give a crystalline mass which was recrystallized from hexane. Yellow crystals of m.p. 72°C, yield 0·7 g (61 per cent) ^1H NMR δ ($CDCl_3$): 0·85 (3 H, t, CH_3–C), 0·89 (3 H, t, CH_3–C), 1·2–1·9 (16 H, m, C–CH_2–C), 2·65 (2 H, t, CH_2–arom), 3·98 (2 H, t, CH_2–O), 4·87 (2 H, s, O–CH_2–CO), 6·58 (1 H, d, H-arom), 6·64 (1 H, d, H-arom), 7·28 (2 H, d, H-arom), 7·71 (2 H, d, H-arom), 7·81 (1 H, d, H-arom). Calculated for $C_{26}H_{36}N_2O_4$: C, 70·09; H, 8·24; N, 6·36 per cent. Found: C, 70·16; H, 8·33; N, 6·24 per cent.

2.1.2. *2-(5-Carboxypentyloxy)-4-hexyloxy-4′-hexylazobenzene*

2-Hydroxy-4-hexyloxy-4′-hexylazobenzene (1·0 g) was treated with 0·84 g tetrahydropyranyl 5-bromohexanoate in a manner similar to the procedure described above to give 1·21 g (94 per cent) orange crystals of m.p. 69°C. ^1H NMR δ ($CDCl_3$): 0·89 (3 H, t, CH_3–C), 0·91 (3 H, t, CH_3–C), 1·2–1·9 (24 H, m, C–CH_2–C), 2·31 (2 H, t, CH_2–arom), 2·68 (2 H, t, CH_2–CO), 4·02 (2 H, t, CH_2–O), 4·13 (2 H, t, CH_2–O), 6·48 (1 H, d, H-arom), 6·58 (1 H, d, H-arom), 7·27 (2 H, d, H-arom), 7·70 (2 H, d, H-arom), 7·80 (2 H, d, H-arom). Calculated for $C_{30}H_{44}H_2O_4$: C, 72·55; H, 8·93; N, 5·64 per cent. Found: C, 72·64; H, 8·99; N, 5·56 per cent.

2.1.3. *2-Benzoyloxy-4-hydroxy-4′-cyanoazobenzene*

To a mixture of 8·3 g concentrated hydrochloric acid and 12 g water was added 3 g of *p*-cyanoaniline under ice-cooling. An aqueous solution of 1·93 g of sodium nitrite in 5 ml water was added dropwise to the mixture below 5°C to afford a diazotized solution. The cooled solution was neutralized with an aqueous sodium carbonate solution and added dropwise to a solution of 5·43 g of resorcin monobenzoate in 50 ml methanol below 10°C. The mixture was neutralized with a saturated aqueous solution of sodium acetate and stirred for 30 min at *c.* 10°C and subsequently for 2 h at room temperature. The precipitate was collected by filtration and washed with water and hexane, followed by drying *in vacuo*. The crude product (8·2 g) was recrystallized from ethyl acetate to yield the azobenzene derivative of m.p. 210°C as orange needles. ^1H NMR δ ($CDCl_3$): 6·83 (1 H, d, H-arom), 6·88 (1 H, d, H-arom), 7·51 (1 H, d, H-arom), 7·62 (5 H, m, H-arom) 7·90 (2 H, d, H-arom). Calculated for $C_{20}H_{13}H_3O_3$: C, 69·98, H; 3·79; N, 12·25 per cent. Found: C, 70·11; H, 3·88; N, 12·09 per cent.

2.1.4. *2-Hydroxy-4-hexyloxy-4′-cyanoazobenzene*

2-Benzoyloxy-4-hydroxy-4′-cyanoazobenzene (3 g) was dissolved in 20 ml DMF and stirred under reflux for 2 h following the addition of 2·4 g hexyl bromide and 2·7 g anhydrous potassium carbonate. To the stirred reaction mixture was added water and was then extracted with hexane. The combined hexane solution was dried over anhydrous sodium sulphate, followed by removal of the solvent. The residual crystalline mass was dissolved in methanol, and the solution was stirred for 3 h at room temperature after addition of 1·0 g potassium hydroxide, and further stirred for 1 h at 50°C with an additional 0·5 g potassium hydroxide. The solution was diluted with water and acidified with hydrochloric acid, followed by extraction with a 1 : 1 mixture of hexane and ethyl acetate. The removal of the solvent from the dried solution gave a crystalline mass which was recrystallized from hexane to yield 33 g of the hydroxyazobenzene. T_{CrN} = 36°C and T_{NI} = 76°C. Calculated for $C_{19}H_{21}N_3O_2$: C, 70·78; H, 6·46; N, 12·9 per cent. Found: C, 71·02; H, 6·74; N, 13·3 per cent. IR (KBr) ν_{max} (cm^{-1}): 2360 (CN). ^1H NMR δ ($CDCl_3$): 0·89 (3 H, t, CH_3–C), 1·2–1·6 (8 H, m, C–CH_2–C), 4·03 (2 H, t, CH_2–O), 6·40 (1 H, d, H-arom), 6·52 (1 H, d, H-arom), 7·59 (1 H, d, H-arom), 7·71 (2 H, d, H-arom), 7·80 (2 H, d, H-arom).

2.1.5. *2-(5-Carboxypentyloxy)-4-hexyloxy-4′-cyanoazobenzene*

To a solution of 2-hydroxy-4-hexyloxy-4′-cyanoazobenzene (2·3 g) in 5 ml DMF was added 0·4 g of tetrahydropyranyl 6-bromohexanoate, 0·2 g of potassium carbonate, and the mixture was stirred for 4 h at 50°C. After removing the precipitates, the filtrate was mixed with hexane and water. The hexane layer was separated and washed thoroughly with water, followed by drying over anhydrous magnesium sulphate. The solution was evaporated to give a residual oil, which was hydrolysed in dioxane containing concentrated hydrochloric acid to yield the carboxylic acid. A crystalline mass was recrystallized from hexane to give 0·25 g of the product of m.p. 110°C. Calculated for $C_{25}H_{31}N_3O_4$: C, 68·66; H, 7·09; N, 9·61 per cent. Found: C, 69·21; H, 7·18; N, 9·57 per cent. ^1H NMR δ ($CDCl_3$): 0·93 (3 H, t, CH_3–C), 1·16–2·07 (14 H, m, C–CH_2–C), 2·41 (2 H, t, CO–CH_2), 4·08 (2 H, t, CH_2–O), 4·18 (2 H, t, CH_2–C), 6·49 (1 H, d, H-arom), 6·57 (1 H, d, H-arom), 7·72 (1 H, d, H-arom), 7·82 (2 H, d, H-arom), 7·91 (2 H, d, H-arom).

2.1.6. *4-Cyano-3′-benzoyloxy-4′-hydroxyazobenzene*

To an aqueous solution of 1·93 g of sodium nitrite in 5 ml water was added 3 g of *p*-cyanoaniline dissolved in a mixture of 8·3 g of concentrated hydrochloric acid and 5 g of water at 5°C. This diazotized solution was added to a methanol (20 ml) solution of 5·43 g of catechol monobenzoate at < 10°C at pH 4–5. A precipitate was recrystallized from aqueous acetone to yield 5 g of the product of m.p. 200°C. Calculated for $C_{20}H_{13}N_3O_3$: C, 69·98; H, 3·79; N, 12·25 per cent. Found: C, 70·77; H, 3·92; N, 12·08 per cent. ^1H NMR δ ($CDCl_3$): 7·19 (1 H, d, H-arom), 7·62 (1 H, d, H-arom), 7·71 (1 H, d, H-arom), 7·89 (5 H, m, H-arom), 7·90 (2 H, d, H-arom), 8·25 (2 H, d, H-arom).

2.1.7. *3-(5-Carboxypentyloxy)-4-hexyloxy-4′-cyanoazobenzene*

A mixture of 1 g of 4-cyano-3′-benzoyloxy-4′-hydroxyazobenzene and 0·5 g of 1-bromohexane in DMF (5 ml) was stirred in the presence of 0·45 g potassium carbonate at 60°C for 2 h, followed by treatment with water to extract a crude product with ethyl acetate. After removing the solvent, an oily residue was dissolved in ethanol, mixed with 5 ml of a concentrated ammonia solution and stirred at 60°C for 2 h, followed by acidification and extraction with dichloromethane. Column chromatography on silica gel was performed to separate 0·57 g 4-cyano-3′-hydroxy-4′-hexyloxyazobenzene as an oil. A DMF (5 ml) solution of 0·38 g of the cyanohydroxyazobenzene and 0·55 g of tetrahydropyranyl 6-bromohexanoate was stirred in the presence of 0·22 g of potassium carbonate to give 0·13 g of the desired product of m.p. 117–119°C after the conventional work-up. Calculated for $C_{25}H_{31}N_3O_4$: C, 68·66; H, 7·09; N, 9·61 per cent. Found: C, 69·01; H, 6·89; N, 10·01 per cent. ^{1}H NMR δ ($CDCl_3$): 0·89 (3 H, t, CH_3–C), 1·25–2·0 (16 H, m, C–CH_2–C), 2·40 (2 H, t, CO–CH_2), 4·11 (4 H, t, CH_2–O), 6·99 (1 H, d, H-arom), 7·55 (1 H, d, H-arom), 7·67 (1 H, d, H-arom), 7·83 (2 H, d, H-arom), 7·94 (2 H, d, H-arom).

2.2. *Preparation of silylating reagents*

2.2.1. *Method A*

An equimolar amount of an azobenzene carboxylic acid was condensed with 3-aminopropyltriethoxysilane in dichloromethane with dicyclohexylcarbodiimide and used for surface modification [3, 5, 6].

2.2.2. *Method B*

2-(10-Carboxydecyloxy)-4-hexyloxy-4′-hexylazobenzene (100 mg) was dissolved in 5 ml benzene containing 5 drops of thionyl chloride and 5 drops of DMF, and the solution was heated at 70°C for 1 h with stirring. After evaporation to dryness, the residual acid chloride was dissolved in a small amount of benzene and added dropwise to a solution of 40 mg of 3-aminopropyltriethoxysilane and 20 mg triethylamine. After evaporating the solvent, the residue was purified by means of column chromatography on silica gel using ethyl acetate as an eluent to yield 121 mg of a crystalline mass. ^{1}H NMR δ ($CDCl_3$): 0·62 (2 H, t, CH_2–Si), 0·89 (3 H, t, CH_3–C), 0·92 (3 H, t, CH_3–C), 1·2–1·9 (32 H, m, C–CH_2–C), 1·24 (9 H, t, CH_3–C), 1·95 (2 H, q, –CH_2–), 2·31 (2 H, t, CH_2–arom), 2·48 (2 H, t, CH_2–CO), 3·23 (2 H, t, CH_2–N), 3·81 (6 H, q, O–CH_2–C), 4·02 (2 H, t, CH_2–O), 4·13 (2 H, t, CH_2–O), 6·48 (1 H, d, H-arom), 6·58 (1 H, d, H-arom), 7·27 (2 H, d, H-arom), 7·70 (2 H, d, H-arom), 7·80 (2 H, d, H-arom).

2.3. *Cell fabrication*

A quartz plate (1 × 3 cm^2) was immersed in an ethanol solution of an azobenzene silylating reagent for 5 min, followed by baking the plate at 120°C for 30 min and by ultrasonical treatment in chloroform for 5 min. This plate was put on another plate surface-modified with lecithin through spherical spacers of 5 μm diameter to assemble a cell, and filled with a nematic LC by capillary action. A guest–host (GH) cell was fabricated by filling with a nematic LC doped with 0·5 wt % of the dichroic dye.

2.4. *Photoirradiation*

The experimental set-up is depicted in our previous papers [6, 7]. The LC cell was placed on a hot stage and exposed vertically to blue light at 443 nm from a 500 W high pressure mercury arc passed through a filter combination of Y-43 and B-46 (Toshiba) and a polarizer. Photoinduced birefringence was monitored by measuring transmitted light intensity of linearly polarized He–Ne laser beam through a cell and a crossed analyser as a function of rotational angle of the cell around the optical axis [6, 7]. Photodichroism of a GH cell was measured by the polarized absorbance at λ_{max} of 625 nm of the diaminoanthraquinone dye (**3**) as a function of rotational angle of the cell around an optical axis using a JASCO U-best spectrometer.

2.5. *Observation of photodichroism of cells*

As described in our previous papers, an LC cell placed on a hot stage was illuminated with a 500 W high pressure Hg arc lamp through a combination of glass filters (Y-43 and B-46: Toshiba) and a polarizer sheet. The photodichroism of an irradiated cell was measured with the use of a JASCO U-best spectrometer by recording the relationship between the absorbance at λ_{max} = 625 nm of the dichroic dye and the rotation angle (ϕ) of the cell to give polar diagrams. The angle ϕ is defined as the angle contained by the polarization plane of the actinic light and that of the measuring light.

3. Results and discussion

3.1. *Structural effect of co-modifiers*

There are at least two requirements for the photoinduced control of azimuthal reorientation of nematic LCs by means of photoactive surface [6]. First, the direction of nematic LC molecules should be parallel with respect to substrate surface to form a planar alignment before and after photoirradiation. Second, the molecular reorientation of photoactive molecules on the surfaces should be induced by linearly polarized light to result in photodichroism on the surfaces without randomization within measuring time for the photoinduced birefringence of the mesophase layer. In our previous work, an azobenzene chromophore (**4a**: C6AzC6-o-C10) (see figure 2) substituted with hexyl and hexyloxy residues at both *para*-positions was designed as a commander molecule to be attached laterally onto a silica surface through a decamethylene spacer to assemble a photoresponsive cell (C10-cell) [6]. Exposure to linearly polarized visible light for the n–π^* transition of the surface azobenzene results in a photo-stationary state containing the corresponding E-isomer as a major component, generating the molecular reorientation to yield a homogeneous alignment.

It has been disclosed that the commanding ability for the homeotropic/planar alignment regulation is influenced not only by the structure of commander molecules on substrate surfaces, but also the average density of the commander molecules [4] and the structure of surface co-modifiers [21]. In order to reveal these factors on the in-plane alignment photocontrol, a silylating reagent of C6AzC6-o-C10 was purified by means of column chromatography to modify a quartz surface with a mixture of the azo-modifier and other silylating reagent in a definite ratio. The condensation of the corresponding azobenzene acid chloride with 3-aminopropyltriethoxysilane was used here because of a higher yield of the desired product.

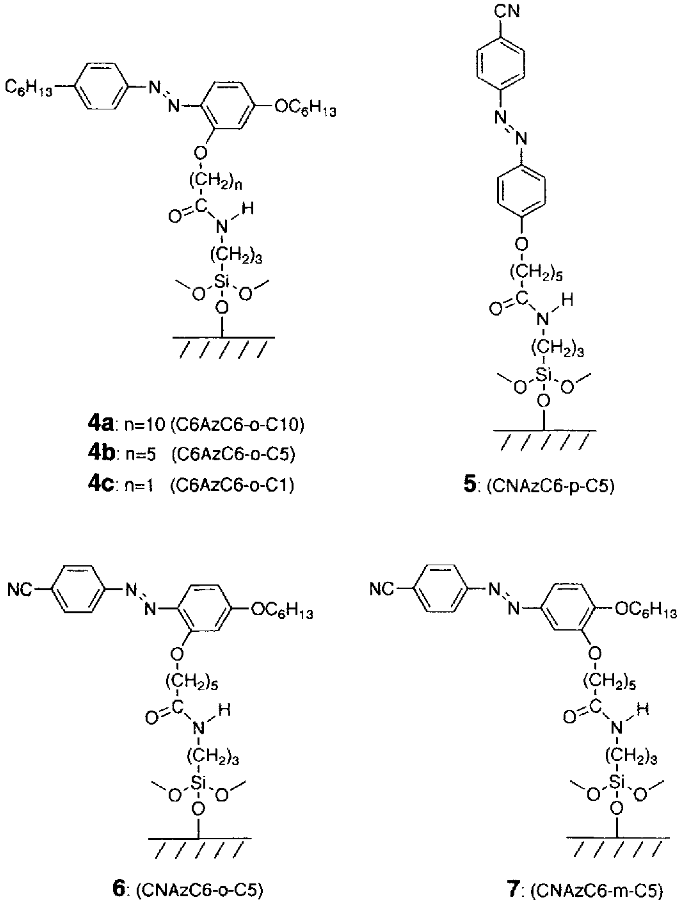

Figure 2. Azo-chromophores on a silica surface.

A quartz surface was modified with C6AzC6-o-C10 in the absence and in the presence of an equimolar amount of a photoinactive silylating reagent like ethyltriethoxysilane (ETS), octadecyltriethoxysilane (ODS) and 3-aminopropyltriethoxysilane (ATS) to be subjected to electronic absorption spectrum measurement before and after UV irradiation. Comparing with the absorption spectrum of the azobenzene in ethanol where approximately 90 per cent of the E-isomer is converted into the Z-isomer under UV irradiation, the conversion into the Z-isomer was reduced on all plates at photostationary states. Approximate contents of the Z-isomer in photostationary states were evaluated by the absorbance for the π, π^* transition and summarized in table 1.

It has been known that the extent of the $E \rightarrow Z$ photoisomerization of azobenzene dissolved in polymeric as well as sol-gel silica matrices is critically influenced by the nature of these matrices so that the azobenzenes are effective photoprobes to elucidate microenvironmental conditions. This leads to reasonable implication that the marked suppression of the $E \rightarrow Z$ photoisomerization on a surface modified solely with C6AzC6-o-C10 may be due to the dense population of the azo-chromophore having two hexyl chains leading to the two-dimensional steric restriction. In particular, a UV-exposed plate modified with a 1 : 1 mixture of the azobenzene and ODS demonstrates only about a half of the $E \rightarrow Z$ conversion, reflecting the steric restriction on the surface owing to the long-alkyl residues. The two-dimensional dilution of the azo-units with both ETS and ATS recovers the sufficient E/Z photoisomerization. This suggests that ethyl and 3-aminopropyl residues, which are both far shorter in length than the spacer linking the chromophore to the surface, assures the photoisomerizability of the azo-units.

Table 1. The content of the Z-isomer at a photostationary state of the azobenzene chemisorbed on a quartz surface.

Molar ratio				
C6AzC6	ETS	ODS	ATS	Z-isomer per cent
1	0	0	0	65
1	1	0	0	70
1	0	1	0	50
1	0	0	1	80
1	—	—	—	90[a]

[a] In ethanol solution.

A hybrid LC cell was fabricated by sandwiching a nematic LC (DON-103) between an azo-modified plate and a plate surface-modified with lecithin for a homeotropic alignment [6]. Linearly polarized light irradiation of the cell was performed at 100°C far above T_{NI} (a transition temperature between nematic and isotropic phases) because of the considerable enhancement of photoalignment by heating as reported previously [6]. In contrast to our previous results [6], an LC cell fabricated with a plate modified solely with purified C6AzC6-o-C10 displayed surprisingly no distinct photoregularity for the in-plane alignment. This difference was thought to be due to the purification of the azo-modifier since in our previous work the azo-silylating reagent was obtained by the DCC coupling of the corresponding azocarboxylic acid and ATS and used for the surface modification without purification. This suggested that the cell owes the commanding ability to the crudity of the azo-silylating reagent contaminated with unreacted ATS. This was confirmed by the fact that a cell worked under polarized light irradiation when a plate was treated with a 1:1 mixture of the purified azo-modifier and ATS or ETS. The suppressive behaviour of the purified azo-silylating reagent is interpreted in terms of a smaller two-dimensional free volume of the azobenzene monolayer, in which the chromophoric reorientation takes place hardly upon exposure to linearly polarized light because of its tight packing on the surface.

3.2. *Spacer length*

A decamethylene spacer was selected first [6], based on our observation that a longer spacer is more favourable for photochemical control of the out-of-plane alignment between homeotropic and planar modes [4]. Here we prepared the azobenzene chromophores substituted with a pentamethylene spacer (**4 b**: C6AzC6-o-C5) and a methylene spacer (**4 c**: C6AzC6-o-C1) to compare the photoregulative function for the LC alignment of DON-103. They were prepared by the DCC coupling of the corresponding carboxylic acid and ATS and used for the surface modification without purification which is rather favourable for the photoalignment regulation, as stated above [6].

The azimuthal photoalignment induced by linearly polarized visible light at 440 nm was confirmed for both LC cells assembled with a plate modified with C6AzC6-o-C5 (C5-cell) and with a plate with C6AzC6-o-C1 (C1-cell). But the emergence of photoinduced birefringence of the LC layer was markedly retarded under illumination at room temperature below T_{NI} just as in the case of the C10-cell modified with C6AzC6-o-C10 [6]. Figure 3 shows the transmitted light intensity of a linearly polarized He–Ne laser beam as a probing light passed perpendicularly through these cells as a function of rotational angle (θ) around the experimental axis after polarized-light irradiation of the cell at 100°C above $T_{NI} = 74°C$. The birefringence measurement was carried out at room temperature. The appearance of peaks and valleys in the transmittance (T) at every 90° interval indicates the uniaxial orientation of the mesophasic layer; T is related with θ according to the following expression:

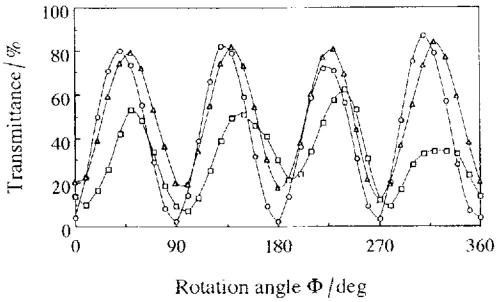

Figure 3. Angular dependence of transmittance of a monitoring He–Ne laser beam passed through an LC cell assembled with a quartz plate modified with **1 a** (C10-cell: ○), **1 b** (C5-cell: △) and **1 c** (C1-cell: □), respectively, after irradiation with linearly polarized light of 445 nm wavelength at 120°C.

$$T = \sin^2 2\theta \sin^2 (\pi \Delta n(\alpha) d/\lambda)$$

where $\Delta n(\alpha)$, d and λ are birefringent index at a tilt angle α, cell thickness and a wavelength of a probing light, respectively. However, there is the difference in the birefringence patterns among the three cells. As seen in figure 3, in contrast to both C5-cell and C10-cell, the regularity in T as a function of θ is distorted for the C1-cell; the transmittances at peaks (T_{max}) and valleys (T_{min}) are not homogeneous. This is due to an incomplete uniformity of the unidirectional alignment of LC. This situation was confirmed by observation of the C1-cell with a polarized microscopy. The microscopic observation revealed also that there are a lot of disclination in the aligned texture, resulting in the partial transmission of the probing light at a crossed position. The relatively large T_{min} values not only for the C1-cell but also for the C5-cell reflects therefore the defects owing to the lack of alignment uniformity and the disclinations. This suggests that the contrast defined as a ratio, $CR = T_{max}/T_{min}$, is a measure of the optical quality of the aligned cells. The CR values for C1-cell, C5-cell and C10-cell were 3·9, 4·8 and 5·0, respectively. From these results, it can be concluded that the spacer length plays an important role in a uniform photoalignment; the longest spacer gives the most homogeneous alignment.

3.3. *Memory effect of surface reorientation*

As stated above and later, heating of a cell above T_{NI} is an effective way to enhance the LC photoalignment.

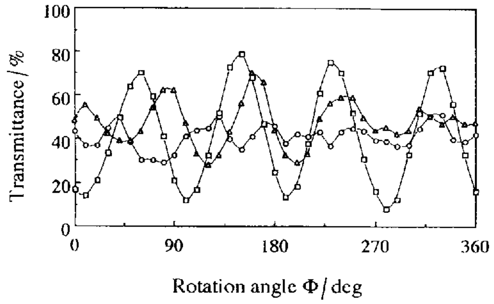

Figure 4. Effect of heat treatment of an EXP-CIL cell (C5-cell) on the in-plane alignment. ○: before irradiation, △: after polarized light irradiation, □: after heating the irradiated cell at 50°C for 30 min.

It was found that this is not always a necessary condition and that the heating after polarized light irradiation is also effective. One of the examples are shown in figure 4 for the C5-cell filled with EXP-CIL. When the C5-cell was exposed to the light first at 25°C, weak birefringence was induced. When the exposed cell was heated subsequently at 50°C above T_{NI} for 30 min, the reorientation of LC was brought about more clearly. This implies that polarized light irradiation induces the reorientation of azobenzene units on a surface although an immature reorientation of surrounding LC molecules at an interface is triggered under the irradiation condition below T_{IN}. Heat treatment of the cell may enhance the mobility of LC molecules to reduce the molecular torque at an interface between the photo-oriented surface and the LC layer. Consequently, the rearrangement of bulk LC molecules is caused by the 'memorized' alignment of the surface azobenzene units.

Closely related phenomenon has been observed in LC polymers substituted with azobenzene moieties in their side chains [22–24]. Though linearly polarized light irradiation results in the photodichroism of azobenzene units in the polymeric matrix, the reorientation of non-photochromic mesogenic units attached to polymeric backbone is hardly brought about till a polymeric layer is heated close to a glass transition temperature (T_g).

3.4. *Photoalignment of GH cells*

In order to obtain further information concerning the in-plane alignment behaviour, a hybrid type guest–host cell (GH cell) was assembled with the use of dichroic diaminoanthraquinone dye (**3**). The azobenzene with decamethylene spacer (C6AzC6-o-C10) as a crude product of the DCC coupling was employed again here because of the good ability for the alignment photocontrol of DON-103, as stated above. The same GH cell was irradiated at 100°C with polarized light having variant polarization angles (θ), followed by measuring dichroism of the doped-dye at room temperature. Figure 5 shows the circular diagrams of polarized absorbances of the dye at 625 nm as a function of angles (ϕ) between a cell axis and the direction of an electric vector of polarized actinic light. The cell axis is defined as the direction of longer sides of a rectangular cell. The maximum absorbances appear at $\phi = \theta \pm \pi/2$, indicating clearly that the direction of the alignment of dye molecules is perpendicular to the polarization plane of the actinic light. This reflects the perpendicular reorientation of an LC director since the direction of a transition moment of the dichroic dye molecules at the visible region is in parallel with that of LC molecules. The dichroic ratios, $R = A_{\parallel}/A_{\perp}$, are apparently independent of the polarization angle θ and show about 5.

The photodichroism induced by the polarized light was extraordinarily stable in line with our previous report on the photoinduced birefringence [6]. No essential alteration in the polar diagram was observable even after heating the cell at 120°C for 1 h and after exposure to non-polarized visible light for 1 h.

Aiming at revealing the effect of two-dimensional diluents on the photoresponsiveness of the cells, substrate plates were treated with crude C6AzC6-o-C10 in the presence of ETS or ODS in a 1 : 9 molar ratio to fabricate hybrid cells (GH-cell-ETS and GH-cell-ODS, respectively) in a manner similar to the cell mentioned

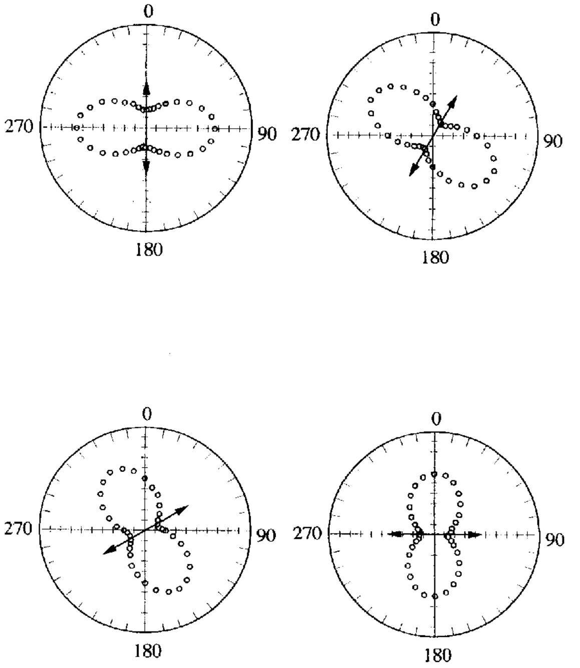

Figure 5. Circular diagrams for the absorbance of a cell filled in with a dye-doped DON-103 (GH cell) at 625 nm as a function of rotational angle (ϕ) of the cell which are exposed to linearly polarized visible light at 100°C. The direction of electric vector of the light is indicated as the arrow.

Table 2. Dichroic ratio of hybrid guest/host cells filled with a nematic LC containing the 0·5 wt % diaminoanthraquinone dye.

Cell	Surface modifier	Polarization angle θ	Dichroic ratio A_{max}/A_{min}
GH cell-1	**4a**	0	4·2
		30	5·1
		60	5·1
		90	4·8
GH cell-2	**4a** + ETS	0	3·8
		45	4·2
		90	4·0
GH cell-3	**4a** + ODS	0	2·1
		45	2·1
		90	2·2

above. Exposure of these GH cells to polarized visible light resulted in the same behaviour; the alignment direction was perpendicular to the polarization plane of the actinic light. However, the dichroic ratio was considerably reduced for the GH cell-ODS which was assembled with a plate modified with a mixture of crude C6AzC6-o-C10 and ODS (see table 2). The suppressive effect of ODS on the photodichroism is assumed to be closely related with the retardation of the *E*/*Z* photoisomerizability of the azo-chromophore on the surface, as discussed previously. The long octadecyl chains sprouting from a surface lower the molecular mobility of the chromophore units to reduce the photoinduced reorientation. Another role of ODS leading to the smaller contrast values is its ability to induce a homeotropic alignment. The presence of such long alkyl chains on the surface brings about the increment of the out-of-plane angle between the surface and molecular axis of LC to lower the absorbance of the dye.

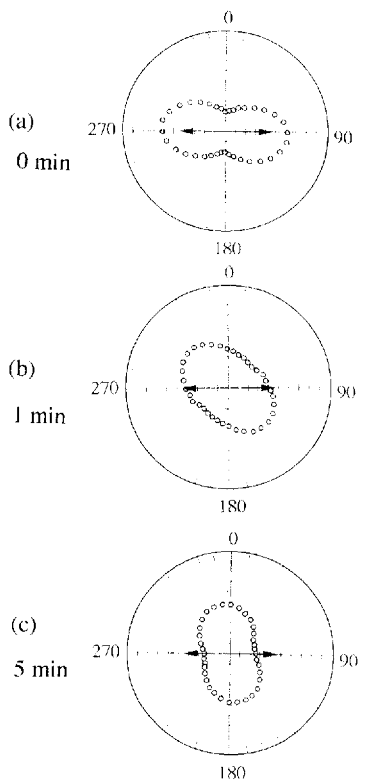

Figure 6. Circular diagrams for the absorbance of a photo-aligned GH cell (GH cell-ETS) at 625 nm as a function of irradiation time with linearly polarized light. (*a*) The cell was irradiated with linearly polarized light at $\theta = 0$ at 50°C in advance to form a homogeneous alignment and irradiated subsequently with the same light for (*b*) 1 min and (*c*) 5 min, respectively, after rotating the polarization plane at $\theta = 90°$. The arrow indicates the direction of electric vector of actinic polarized light.

3.5. *Photoinduced reorientation*

As shown in figure 5, polarized light irradiation with sufficient energy caused a perpendicular reorientation of LC. This process was reversible. Photoinduced LC reorientation of the GH cell was followed by measuring polar diagrams of the doped dye during the polarized irradiation. The polar diagrams representing the photodichroism of GH cell-ETS as a typical example is illustrated in figure 6. The direction of the dye alignment is rotated gradually as the exposure time advanced, although the shape of the circular diagram is distorted slightly to show the reduction of the dichroic ratio during the irradiation.

The rate for the photoinduced reorientation of LC molecules was measured according to the following procedure. The hybrid cells were initially illuminated with the polarized light at 120°C for the homogeneous alignment. They were subsequently exposed to the light at various temperatures after rotating the polarization plane 90°C. The angular dependence of an absorbance at 625 nm was recorded at intervals at room temperature as a function of the cell direction to give polar diagrams, as shown in figure 6 as an example, for the determination of the alignment direction. Three types of GH cell were used; GH cell, GH cell-ETS and GH cell-ODS. Here, a reorientational angle (δ) is defined as an angle between the directions of a homogeneous alignment before and after subsequent irradiation. δ values are plotted against the exposure energies of linearly polarized visible light and presented in figures 7, 8 and 9, respectively. The results for the reorientational behaviours of the three cells are summarized as follows. First, the alignment reorientation induced by polarized light irradiation is strongly dependent on a cell temperature and accelerated markedly by heating above T_{NI} (= 72°C). Second, the rate of the reorientation is affected by the nature of the azo-modification; the surface modification with ETS results in the effective LC reorientation at 70°C slightly

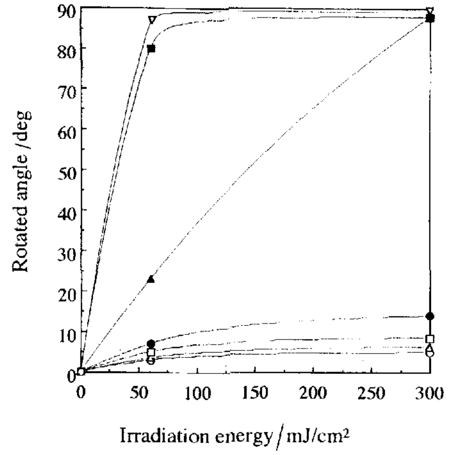

Figure 7. Rotational angles of the aligned direction of the dichroic dye (3) dissolved in DON-103 which was filled in a cell (GH cell) as a function of exposure energy of 445 nm polarized light. The cell was heated during the irradiation at 35°C (○), 40°C (△), 50°C (□), 60°C (●), 70°C (▲), 80°C (■) and 120°C (▽), respectively.

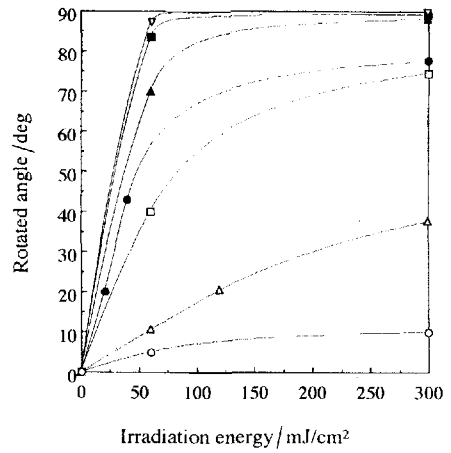

Figure 8. Rotational angles of the aligned direction of the doped dichroic dye (3) dissolved in DON-103 which was filled in a cell (GH cell-ETS) as a function of exposure energy of 445 nm polarized light. The cell was heated during the irradiation at 35°C (○), 40°C (△), 50°C (□), 60°C (●), 70°C (▲), 80°C (■) and 120°C (▽), respectively.

lower than T_{NI} while an ODS plate causes the retardation of the reorientation at the same temperature. Third, the reorientation is almost saturated at an exposure energy of about 100 mJ cm^{-2} irrespective of the surface nature when the cell are heated above T_{NI}.

A very thin film mesophasic layer on a substrate is thought to possess higher orderedness than that of a bulk nematic layer and forms a smectic-like phase [25]. This may be closely related to our observation. Heating of the cell brings about the increase in the mobility of LC molecules at an interface to enhance the photoinduced LC reorientation. The effect of the alkyl co-modifiers may be interpreted in terms of two-dimensional free volume, just as discussed above. ODS residues tethered from the surface is much longer than the decamethylene spacer anchoring the azo-moiety on the surface to retard the photoinduced reorientation of azo-chromophores owing to the steric hindrance while ethyl residues are no obstacle to the photoinduced reorientation of the chromophore.

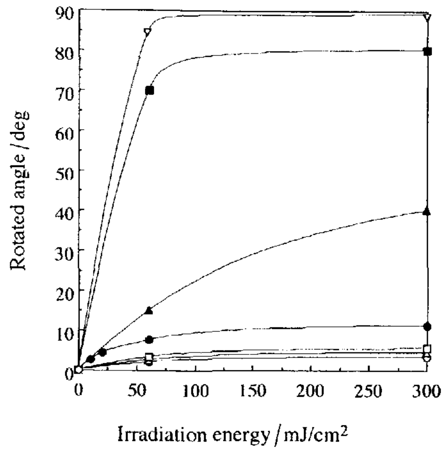

Figure 9. Rotational angles of the aligned direction of the doped dichroic dye (3) dissolved in DON-103 which was filled in a cell (GH cell-ODS) as a function of exposure energy of 445 nm polarized light at 35°C (○), 40°C (△), 50°C (□), 60°C (●), 70°C (▲), 80°C (■) and 120°C (▽), respectively.

Exposure energies for the reorientation is markedly smaller than those for other surface-modified LC photoalignment using polymeric thin films which require more than a few J cm^{-2} [8, 10, 17]. Our recent work has revealed that the polarized-light-induced reorientation of azo-chromophores in a thin film of vinyl polymers is complete within about 100 mJ cm^{-2} of exposure energies before cell assemblage although a few J cm^{-2} exposure energy is needed when the surface is covered with LC molecules [15]. Similar results were obtained when a substrate surface was covered with a monolayer of a polyimide bearing p-cyanoazobenzene [26]. In other words, the photosensitivity of azo-units on a topmost surface for the LC reorientation is much retarded by the contact with LC molecules. This implies that the micro-environmental conditions of azo-commander residues on a surface layer of polymeric films is prominently modified probably by the formation of supramolecular aggregates composed of the azo-units and LC molecules. Because of the capability for LC molecules to penetrate into polymer films [14], azo-chromophores are probably surrounded by LC molecules at least at a surface layer. Photoresponsive behaviours of azo-modified polymeric LCs should be mentioned in this context. This type of polarized-light sensitive systems forms supramolecular structures consisting of azo-moieties and mesogenic units, both of which are bound to polymeric backbones covalently. Usually, much large exposure energy is required to cause the emergence of birefringence of a polymeric film due to the polarized-light-induced molecular reorientation [22–24] whereas the heating at temperatures close to T_g of LC polymers enhances the photoinduced reorientation drastically [24(*b*)]. These results suggest that the behaviours of azo-chromophores at a polymeric surface in contact with low mass LCs is similar to that of bulk polymeric LCs substituted with azo-moieties. In contrast to polymeric films, a silica matrix inhibits thoroughly the penetration of LC molecules because of tightly crosslinked networks so that molecular interactions of azo-chromophores with low mass LC molecules give rise to only a two-dimensional organizate at an interface. Probably such monolayered aggregates assure the mobility of LC molecules to result in quicker photoresponse.

3.6. *Effect of positional isomerism*

The effect of positional isomerism of azobenzene on the LC photoregulation is an interesting subject in respect to a molecular design of commanders. Since a *p*-alkylazobenzene results in a homeotropic alignment when the chromophore is attached to a silica surface through silylation at its opposite *para*-position [4], *p*-alkyl substituent is inadequate to determine the positional effect on the in-plane alignment photoregulation. Fortunately, as described in our previous papers, *p*-cyanoazobenzene is able to command the LC in-plane alignment regulation upon exposure to linearly polarized light even though the chromophore is bound onto a silica surface at its opposite *para*-position using a crude silylating reagent of CNAzC6-p-C5 (**5**) [6] (see figure 2). The effectiveness of the *p*-cyanoazobenzene unit was confirmed further by the fact that the in-plane photoregulation of LC alignment is achieved by a monolayer of a polyimide incorporating *p*-cyanoazobenzene in the main chain [26]. It follows that a triethoxy residue was introduced at the *ortho*- and *meta*-position of the chromophore to prepare two isomeric silylating reagents (**6** and **7**), respectively, to attach the commander molecule laterally to a silica surface [27].

Electronic absorption spectra of three isomers in ethanol and on quartz plates are shown in figure 10. The absorption coefficients of the *ortho*- and *meta*-isomers at around 380 nm for the π, π^* transition are considerably reduced in solution as compared with that of the *para*-isomer because of the decrease in the molecular symmetry (see table 3). As a result, the absorbances (A_L) at the longer wavelength in the *meta*- and *ortho*-isomers are smaller than those (A_S) at *c.* 270 nm. On the contrary, A_L is enhanced for both isomers when they are attached to quartz plates. A ratio (A_L/A_S) of absorbance of azo-chromophores at the shorter wavelength to that at longer wavelength is a measure of the orientation of the dichroic molecules on a surface since A_L is assignable to the transition moment in parallel with the longer molecular axis whereas A_S is due to the transition moment perpendicular to the molecular axis. In fact, our recent work revealed that the (A_L/A_S) ratio of a *p*-alkylazobenzene attached to a surface of a quartz plate through a silylation is markedly reduced when the surface is wetted with a nematic LC as a result of cooperative work of the LC leading to a perpendicular reorientation of the azo-chromophore on the surface [28]. It is reasonable to conclude that the enhancement of the (A_L/A_S) ratio of both *meta*- and *ortho*-isomers suggests that the azobenzene molecules orient favourably in parallel to the quartz surface. By contrast, the orientation of the *para*-isomer derived from CNAzC6-p-C5 (**5**) on the plate surface is randomized since the absorption

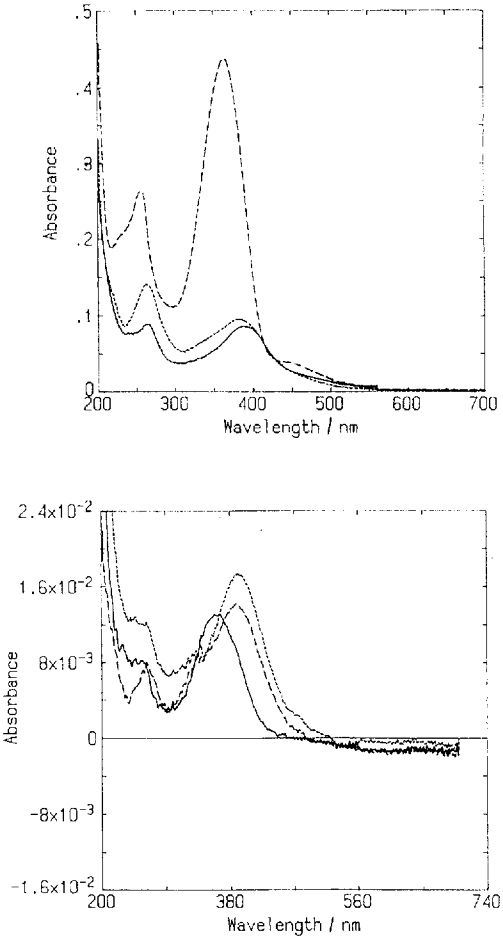

Figure 10. Electronic absorption spectra of *p*-cyanoazobenzenes in ethanol (upper panel) and attached to a quartz plate surface (lower panel). ——: CNAzC6-p-C5, ······: CNAzC6-m-C5, – – –: CNAz6-o-C5.

Table 3. Absorption spectral properties of *p*-cyanoazobenzene[a].

	In ethanol			On quartz surface		$(A_L/A_S)_{sol}$
Isomer	λ_{max}/nm	ε/dm^2 mol^{-1}	$(A_L/A_S)_{sol}$	λ_{max}/nm	$(A_L/A_S)_{sur}$	$(A_L/A_S)_{sur}$
para-	365	18100	1·58	365	1·58	1·00
meta-	379	11500	0·68	382	1·77	0·38
ortho-	387	9100	0·98	389	1·41	0·70

[a] $(A_L/A_S)_{sol}$ and $(A_L/A_S)_{sur}$ denote the ratios of absorbances at longer (A_L) and shorter (A_S) wavelengths in an ethanol solution and on a quartz plate, respectively.

spectrum is quite similar to that in an ethanol solution. The latter situation allows us to estimate the average density of the *p*-azobenzene on the surface spectroscopically. The density was calculated to be 1·7 azo-chromophores in 1 nm^2 with the use of the absorption coefficient ($\varepsilon = 18\,100$) at λ_{max}. The estimation of the average density of the *ortho-* and *meta*-isomers, derived from CNAzC6-o-C5 (**6**) and CNAzC6-m-C5 (**7**), on the surface through the same procedure was not achieved because of the distorted ε-values due to the parallel conformation of the chromophore on the surface.

All of LC cells fabricated with quartz plates treated with these *p*-cyanoazobenzenes demonstrated a homogeneous alignment under irradiation with linearly polarized visible light. In this experiment, a nematic LC (EXP-CIL) with the lower $T_{NI} = 31·5°C$ was employed instead of DON-103 in order to achieve the photoalignment at temperatures close to an ambient temperature. It was found that the irradiation energy of polarized light for the LC reorientation is strikingly influenced by the positional isomerism. The photoinduced reorientation was determined as follows. The whole area of a cell was exposed to polarized light and subsequently illuminated with the same light after rotating the polarization plane 45°. The direction of the alignment was monitored by measuring the transmittance of probing light at room temperature below T_{NI} as a function of rotational angle of the cell, just in the case of GH cells described above. The results are shown in figures 11, 12 and 13, respectively, for the *para-*, *ortho-* and *meta*-isomers and summarized as follows. First, the rate of the LC reorientation is again temperature-dependent so that the heating above T_{NI} is favourable for the reorientation. Second, the reorientational angle (δ) induced by the *para*-isomer does not attain 45° (see figure 11) whereas both *meta-* and *ortho*-isomers result in the complete rotation (see figures 12 and 13). Third, the *meta*-isomer displays the highest sensitivity, and the reorientation is complete at an irradiation energy of about only 10 mJ cm^{-2} (see figure 13). It should be stressed that this exposure energy is considerably small, as compared with the photoalignment by means of thin films of azo-polymers [8, 10, 17], as stated above. As shown in table 3, the *meta*-attach-

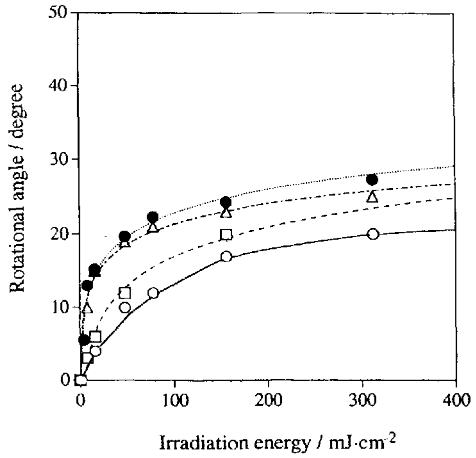

Figure 11. Reorientational angles of the aligned direction of EXP-CIL filled in a cell surface-modified with CNAzC6-p-C5 as a function of exposure energy of 445 nm polarized light. The cell was irradiated at 25°C (○), 30°C (□), 45°C (△) and 60°C (●), respectively.

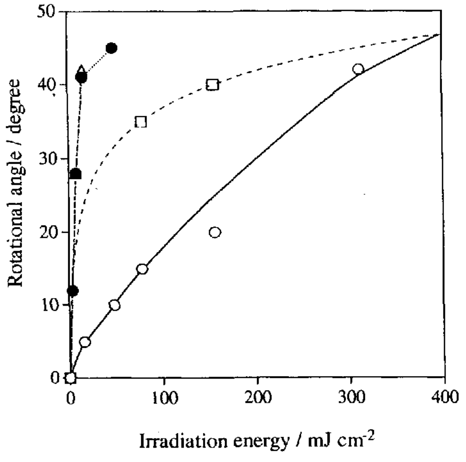

Figure 12. Reorientational angles of the aligned direction of EXP-CIL filled in a cell surface-modified with CNAzC6-o-C5 as a function of exposure energy of 445 nm polarized light. The cell was irradiated at 25°C (○), 30°C (□), 45°C (△) and 60°C (●), respectively.

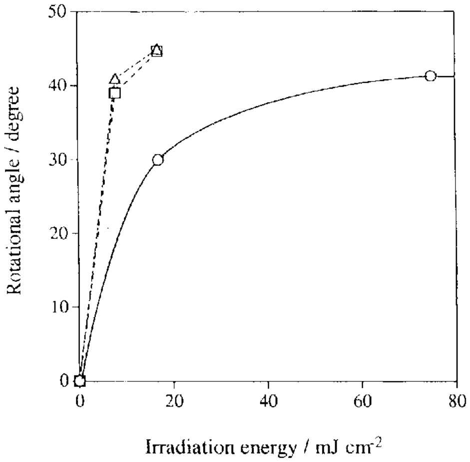

Figure 13. Reorientational angles of the aligned direction of EXP-CIL filled in a cell surface-modified with CNAzC6-m-C5 as a function of exposure energy of 445 nm polarized light. The cell was irradiated at 25°C (○), 30°C (□) and 45°C (△), respectively.

ment of the azo-chromophore resulted in the most remarkable reduction of the (A_L/A_S) value among three types of the isomerism. This means that the *p*-cyanoazobenzene attached to a quartz surface at the *meta*-position is aligned most favourably parallel to the surface so that the 'molecular rotor' works smoothly.

These results all confirm that the lateral (side-on type) attachment of the azo-chromophore to a silica surface provides higher efficiency of the photoalignment and that the concept of 'molecular rotor' [6] on a substrate surface affords a novel way to enhancement of alignment photoregularity by the command surfaces.

4. Conclusions

The in-plane LC alignment driven by irradiation with linearly polarized visible light was markedly influenced by molecular structures of azo-chromophores chemisorbed on a surface of a silica plate and is summarized as follows.

(i) The surface density of the azo-chromophore plays a critical role in the photoregulation. Two-dimensional dilution of the chromophore with ETS or ATS of a shorter organic residue gives better results so that a crude silylating reagent contaminated with ATS is rather favourable for the present purpose.

(ii) The second factor affecting the photoalignment is the length of a spacer attaching the azo-units to a silica surface; a longer spacer is more favourable.

(iii) The co-modification with an inert silylating reagent influences the efficiency of the in-plane alignment photoregulation. The co-existence of octadecyl residue interrupts not only the *E/Z* photoisomerizability of the surface azobenzene, but also the polarized-light-induced reorientation of liquid crystals.

(iv) Irradiation energy for the LC reorientation is considerably dependent on the positional isomerism of 4-cyano-4′-hexyloxyazobenzene. A command surface covered with the *meta*-isomer exhibits the highest photosensitivity; exposure energy of *c.* $10\,\mathrm{mJ\,cm^{-2}}$ results in the LC reorientation.

All these results stress that the molecular design of commander molecules plays a very important role in the in-plane alignment photoregulation.

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