
**Liquid Crystals**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

# In situ photochemical conversion from cinnamoyl-functionalized liquid-crystalline monomers to liquid-crystalline dimers

Hideyuki Kihara[a]; Nobuyuki Tamaoki[a]
[a] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

**To cite this Article** Kihara, Hideyuki and Tamaoki, Nobuyuki(2007) 'In situ photochemical conversion from cinnamoyl-functionalized liquid-crystalline monomers to liquid-crystalline dimers', Liquid Crystals, 34: 11, 1337 — 1347
**To link to this Article: DOI:** 10.1080/02678290701697454
**URL:** http://dx.doi.org/10.1080/02678290701697454

*Liquid Crystals*, Vol. 34, No. 11, November 2007, 1337–1347



# *In situ* photochemical conversion from cinnamoyl-functionalized liquid-crystalline monomers to liquid-crystalline dimers

HIDEYUKI KIHARA* and NOBUYUKI TAMAOKI

Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

(*Received 25 July 2007; accepted 21 September 2007*)

Liquid-crystalline (LC) monomers, which were functionalized with a cinnamoyl group on their extremity, were synthesized and irradiated with UV light in their LC phases. In the presence of a triplet sensitizer, most LC monomers were converted into the corresponding dimers, which were produced by the cycloaddition reaction of the cinnamoyl group. The photodimerization reaction could proceed while the LC phases were maintained, because the dimers showed LC phases whose temperature ranges were wider than those of the corresponding monomers. A $^1$H NMR study of the LC dimers indicated that the cyclobutane unit dominantly had an *anti*-head-to-head configuration, that is, $\delta$-truxinate. As the LC monomers, which had a phenyl biphenyl-4-carboxylate moiety as a mesogen, showed smectic A phases and the corresponding dimers also exhibited smectic A phases, we estimated the smectic layer distances by X-ray diffraction analysis and found that the dimers adopted the structure in which the two mesogens aligned laterally and existed in the same smectic layer in the LC phases.



## 1. Introduction

The introduction of a cinnamoyl group to liquid-crystalline (LC) materials is of great interest because the properties of LC materials can be modified *in situ* by means of an easily manipulated stimulus: light. For instance, to modify LC polymers, the photodimerization of a cinnamoyl group has been used for the fixation or cross-linking of the LC phase structures [1–3] and for the alignment control of low-molecular-weight liquid crystals spread on the LC polymers [4–6]. The reaction was also used for the polymerization of discotic LC compounds [7, 8] and a LC dendrimer [9] in their LC phases. In the case of monocinnamoyl-functionalized LC monomers, the photodimerization was investigated in order to determine the effects of the LC ordering field on the reaction [10, 11].

When a dicinnamoyl-functionalized LC monomer is photodimerized, it is theoretically possible to obtain linear LC polymers if the reaction takes place intermolecularly. Actually, a few groups of researchers, including ours, photoirradiated dicinnamoyl-functionalized LC monomers [12–14], but only our group could obtain the oligomer that showed a LC phase [14]. We attributed our success to the adequate molecular design of the LC monomer, in which the two cinnamoyl moieties were introduced on each molecular end, and the separation of the moieties from a relatively large mesogen by an alkylene spacer.

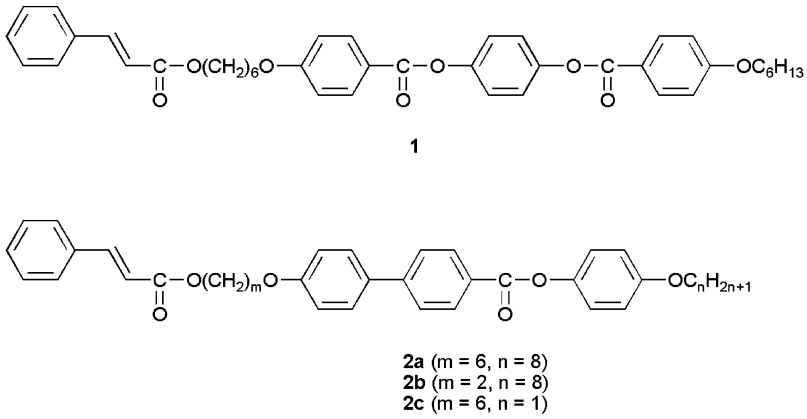
Here, we have prepared new monocinnamoyl-functionalized LC monomers according to the above-mentioned molecular design. Their chemical structures are shown in scheme 1. LC compound **1** has a 1,4-bis(benzoyloxy)benzene as a mesogen, which is the same as used for the bifunctional LC monomer [14], whereas LC compounds **2a–c** have a phenyl biphenyl-4-carboxylate as a mesogen, which we used because we expect that the compounds show smectic LC phases [15].

As mentioned above, a monocinnamoyl-functionalized LC compound, a cholesteryl cinnamate, was photodimerized [10, 11]. In [10, 11], however, the dimer was neither isolated nor well characterized, and there was no mention of whether the reaction mixture maintained the LC phase during photoirradiation. In the present study, we attempt to obtain the dimers, which can be well characterized and show thermally stable LC phases, so that we can convert LC monomers to LC dimers *in situ*.

An investigation of the photodimerization of the monocinnamoyl-functionalized LC monomers **1** and **2a–c** will provide us with new knowledge about the photopolymerization of the bifunctional LC monomer

*Corresponding author. Email: h-kihara@aist.go.jp

*Liquid Crystals*
ISSN 0267-8292 print/ISSN 1366-5855 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290701697454




Scheme 1. The chemical structures of monomers **1** and **2a–c**.

we studied previously [14], because the photodimerization of the monomers **1** and **2a–c** is considered to be a model for photopolymerization. In addition, the LC dimers themselves are worth investigating. They have attracted much attention because they show rich and unusual mesomorphism [16], such as a significant odd–even effect in clearing temperatures [17], smectic polymorphism [18] and antiferroelectricity [19], which is different from that of LC monomers. Recently, it has been reported that the LC dimers with an $\alpha,\omega$-diiminoalkylene spacer show smectic phases or a $B_6$ phase, depending on the parity of the spacer [20]. In this study, we measure smectic layer distances of the LC monomer and the corresponding dimer that show smectic phases and compare them in order to estimate the conformation of the dimer in the LC phase.



## 2. Experimental details

### 2.1. *Materials*

All solvents and reagents were obtained from commercial sources and were used without further purification unless otherwise noted.

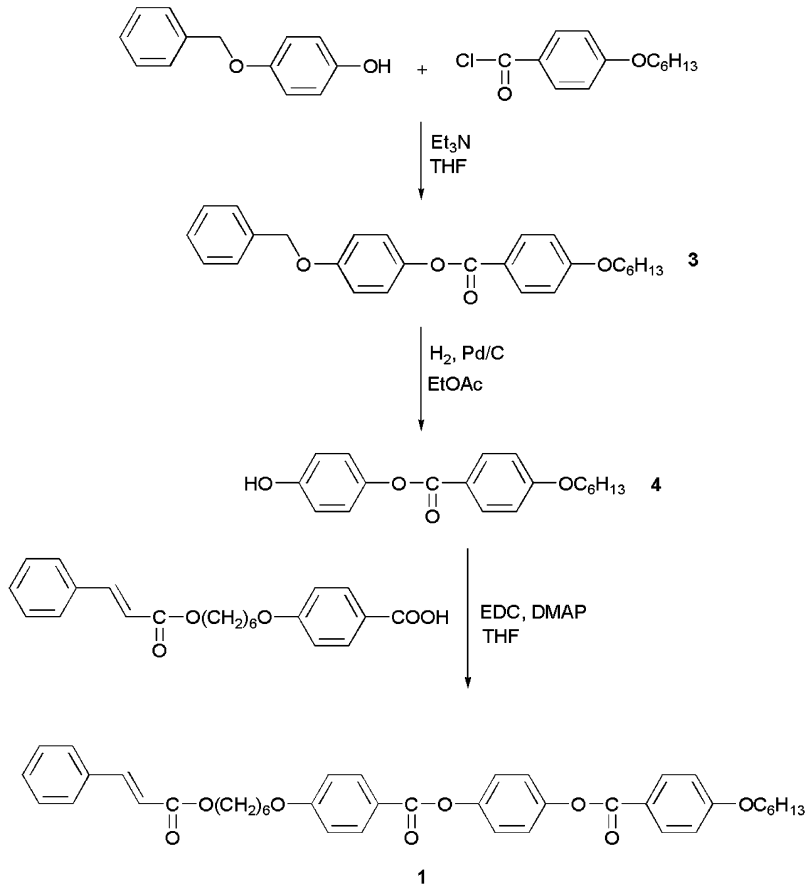
### 2.2. *Synthesis*

The routes of **1** and **2a–c** synthesis are shown in schemes 2 and 3, respectively. The details are described in the following.

**2.2.1. 4-Benzyloxyphenyl 4-hexyloxybenzoate (3).** 4-Benzyloxyphenol (1.7 g, 8.3 mmol) and $Et_3N$ (1.4 ml) were dissolved in 30 ml of dry tetrahydrofuran (THF). After cooling of the solution to 0°C in a $N_2$ atmosphere, 20 ml of dry THF containing 4-hexyloxybenzoyl chloride (2.0 g, 8.3 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 20 h and then poured into 5% $NaHCO_3$ (aqueous). The resulting mixture was extracted three times with 100 ml of dichloromethane. The combined dichloromethane was washed with water, dried over $MgSO_4$, filtered and concentrated. The crude product was purified by recrystallization from EtOH to give **3** (2.7 g, 81%) as white crystals: melting point 121°C (94°C, monotropic nematic phase); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.92 (t, 3H, $J$=6.9 Hz), 1.36 (m, 4H), 1.49 (m, 2H), 1.82 (m, 2H), 4.04 (t, 2H, $J$=6.5 Hz), 5.07 (s, 2H), 6.96 (d, 2H, $J$=8.9 Hz), 7.00 (d, 2H, $J$=9.1 Hz), 7.11 (d, 2H, $J$=9.1 Hz), 7.31–7.46 (m, 5H), 8.12 (d, 2H, $J$=8.9 Hz).

**2.2.2. 4-Hydroxyphenyl 4-hexyloxybenzoate (4).** A mixture of **3** (2.5 g, 6.2 mmol) and 5% Pd/C (0.25 g) in ethyl acetate (100 ml) was vigorously stirred under a $H_2$ atmosphere with a slightly positive pressure for 20 h. The reaction mixture was filtered through a Celite pad and the combined filtrate was evaporated under reduced pressure. The crude residue was purified by column chromatography (silica gel; eluent: hexane/ethyl acetate=3/2) to obtain **4** (1.8 g, 91%) as a white solid: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.92 (t, 3H, $J$=6.9 Hz), 1.36 (m, 4H), 1.49 (m, 2H), 1.82 (m, 2H), 4.04 (t, 2H, $J$=6.5 Hz), 5.58 (s, 1H), 6.78 (d, 2H, $J$=9.0 Hz), 6.96 (d, 2H, $J$=9.0 Hz), 7.01 (d, 2H, $J$=9.0 Hz), 8.13 (d, 2H, $J$=9.0 Hz).

**2.2.3. 4-(4-(Hexyloxy)benzoyloxy)phenyl 4-(6-(cinnamoyloxy)hexyloxy)benzoate (1).** A mixture of **4** (1.8 g, 5.7 mmol), 4-(6-(cinnamoyloxy)hexyloxy)benzoic acid (2.1 g, 5.7 mmol), which was prepared according to the procedure described in a previous paper [14], and DMAP (0.1 g, 0.8 mmol) was dissolved in 40 ml of dry THF. While the mixture was stirred at room temperature under a $N_2$ atmosphere, 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC; totalling 1.2 g, 6.2 mmol) was added portionwise for 10 min. After stirring for 24 h at room temperature, the mixture



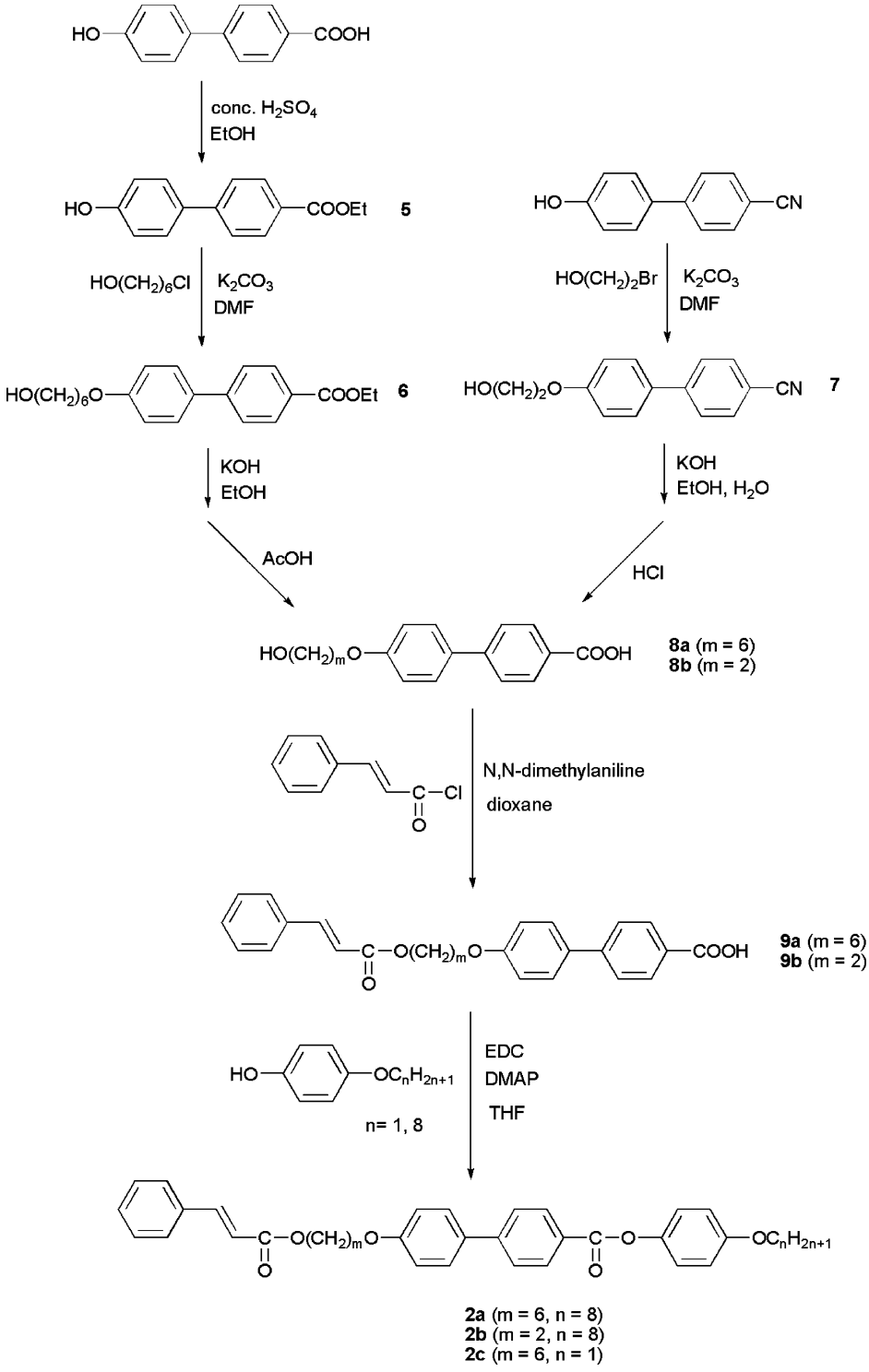

Scheme 2. Route of synthesis of monomer **1**.



was poured into 200 ml of water containing 4 g of $NH_4Cl$ and extracted three times with 100 ml of dichloromethane. The combined dichloromethane layers were washed with water, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, eluent was dichloromethane) and recrystallization from a mixture of EtOH and toluene to afford **1** (2.8 g, 74%) as white crystals: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.92 (t, 3H, J=6.9 Hz), 1.37 (m, 4H), 1.54 (m, 6H), 1.75–1.89 (m, 6H), 4.03–4.09 (m, 4H), 4.24 (t, 2H, $J$=6.6 Hz), 6.45 (d, 1H, $J$=16.0 Hz), 6.97 (d, 4H, $J$=8.9 Hz), 7.25 (s, 4H), 7.38 (m, 3H), 7.51–7.54 (m, 2H), 7.69 (d, 1H, $J$=16.0 Hz), 8.13 (d, 2H, $J$=8.9 Hz), 8.14 (d, 2H, $J$=8.9 Hz); MALDI-TOFMS ($M$+Na=687.77) $m/z$ 687.6 $[M+Na]^+$.

**2.2.4. Ethyl 4′-hydroxy-4-biphenylcarboxylate (5).** 4′-Hydroxy-4-biphenylcarboxylic acid (20 g, 93 mmol) was dissolved in 250 ml of EtOH. After the addition of concentrated $H_2SO_4$ (20 ml), the EtOH solution was refluxed with stirring for 6 h. After cooling, the reaction mixture was concentrated to around 50 ml by rotary evaporator and poured into 500 ml of water. The precipitate was collected by filtration and recrystallized from EtOH to afford **5** (19.6 g, 87%) as white crystals: melting point 141°C; $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.42 (t, 3H, $J$=7.0 Hz), 4.41 (q, 2H, $J$=7.0 Hz), 6.95 (d, 2H, $J$=8.4 Hz), 7.52 (d, 2H, $J$=8.4 Hz), 7.61 (d, 2H, $J$=8.4 Hz), 8.09 (d, 2H, $J$=8.4 Hz).

**2.2.5. Ethyl 4′-(6-hydroxyhexyloxy)-4-biphenylcarboxylate (6).** A mixture of **5** (10 g, 41 mmol), 6-chloro-1-hexanol (6.8 g, 50 mmol), $K_2CO_3$ (11.4 g) and dimethylformamide (DMF; 50 ml) was stirred at 120°C for 4 h under a $N_2$ atmosphere. After cooling, the mixture was poured into 300 ml of water and extracted three times with chloroform. The combined chloroform was washed with water, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by recrystallization from EtOH to give **6** (11.9 g, 84%) as white crystals: $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.41 (t, 3H, $J$=7.0 Hz), 1.49 (m, 4H), 1.62 (m, 2H), 1.83 (m, 2H), 3.67 (t, 2H, $J$=6.5 Hz), 4.00 (t, 2H, $J$=6.5 Hz), 4.39 (q, 2H, $J$=7.0 Hz).




Scheme 3. Routes of synthesis of monomers **2a–c**.

**2.2.6. 4′-(2-Hydroxyethoxy)-4-cyanobiphenyl (7).** A mixture of 4′-hydroxy-4-cyanobiphenyl (9.4 g, 48 mmol), 2-bromoethanol (7.2 g, 57.6 mmol), $K_2CO_3$ (13.3 g) and DMF (40 ml) was stirred at 120°C under an $N_2$ atmosphere for 24 h. After cooling, the mixture was poured into 300 ml of water and extracted three times with dichloromethane. The combined dichloromethane was washed with water, dried over $MgSO_4$, filtered and

evaporated under reduced pressure. The residue was purified by recrystallization from a mixture of ethyl acetate and hexane to give **7** (2.4 g, 21%) as white crystals: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 2.08 (br t, 1H), 4.00 (m, 2H), 4.15 (t, 2H, $J$=4.8 Hz), 7.03 (d, 2H, $J$=8.8 Hz), 7.54 (d, 2H, $J$=8.8 Hz), 7.64 (d, 2H, $J$=8.6 Hz), 7.70 (d, 2H, $J$=8.6 Hz).

**2.2.7. 4′-(6-Hydroxyhexyloxy)-4-biphenylcarboxylic acid (8a).** A mixture of **6** (5.0 g, 14.6 mmol), KOH (2.9 g) and EtOH (40 ml) was refluxed with stirring for 3 h. During the reaction, precipitates were observed. After cooling, the precipitates were collected by filtration and recrystallized from a mixture of acetic acid and ethanol to give **8a** (3.7 g, 81%) as white crystals: $^1$H NMR (270 MHz, DMSO-$d_6$) $\delta$ 1.42 (m, 6H), 1.73 (m, 2H), 3.40 (m, 2H), 4.01 (t, 2H, $J$=6.5 Hz), 4.4 (br t, 1H), 7.4 (d, 2H, $J$=8.6 Hz), 7.68 (d, 2H, $J$=8.6 Hz), 7.75 (d, 2H, $J$=8.1 Hz), 7.98 (d, 2H, $J$=8.1 Hz).

**2.2.8. 4′-(2-Hydroxyethoxy)-4-biphenylcarboxylic acid (8b).** A mixture of **7** (2.4 g, 10.0 mmol), KOH (14 g), EtOH (50 ml) and $H_2O$ (30 ml) was refluxed with stirring for 10 h. After cooling, the reaction mixture was poured into 200 ml of water and acidified with 5% HCl (aqueous) to precipitate the reacted product. The crude product was purified by recrystallization from ethanol to afford **8b** (1.6 g, 62%) as white crystals: $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 3.74 (t, 2H, $J$=4.8 Hz), 4.05 (t, 2H, $J$=4.8 Hz), 7.06 (d, 2H, $J$=8.7 Hz), 7.68 (d, 2H, $J$=8.7 Hz), 7.75 (d, 2H, $J$=8.2 Hz), 7.98 (d, 2H, $J$=8.2 Hz).

**2.2.9. 4′-(6-(Cinnamoyloxy)hexyloxy)-4-biphenylcarboxylic acid (9a).** A mixture of **8a** (3.0 g, 9.5 mmol) and N,N-dimethyaniline (1.3 g, 11.0 mmol) was dissolved in 40 ml of dioxane. To the stirred solution, 10 ml of dioxane containing cinnamoylchloride (1.8 g, 11 mmol) was added dropwise at 80°C. The reaction mixture was stirred at 90°C for another 5 h. After cooling, the mixture was poured into 300 ml of water and extracted three times with chloroform. The combined chloroform was washed with water, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by recrystallization from a mixture of ethanol and dioxane to obtain **9a** (2.8 g, 65%) as white crystals: $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 1.54 (m, 4H), 1.77 (m, 2H), 1.85 (m, 2H), 4.03 (t, 2H, $J$=6.3 Hz), 4.24 (t, 2H, $J$=6.5 Hz), 6.45 (d, 1H, $J$=16.2 Hz), 6.99 (d, 2H, $J$=8.9 Hz), 7.38 (m, 3H), 7.52 (m, 2H), 7.57 (d, 2H, $J$=8.9 Hz), 7.65 (d, 2H, $J$=8.1 Hz), 7.69 (d, 1H, $J$=16.2 Hz), 8.15 (d, 2H, $J$=8.1 Hz).

**2.2.10. 4′-(2-(Cinnamoyloxy)ethoxy)-4-biphenylcarboxylic acid (9b).** This was obtained in 20% yield from **8b** and cinnamoyl chloride by following the procedure for **9a**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.32 (t, 2H, $J$=4.7), 4.60 (t, 2H, $J$=4.7), 6.50 (d, 1H, $J$=16.0 Hz), 7.05 (d, 2H, $J$=8.8 Hz), 7.39 (m, 3H), 7.53 (m, 2H), 7.60 (d, 2H, $J$=8.8 Hz), 7.66 (d, 2H, $J$=8.5 Hz), 7.73 (d, 1H, $J$=16.0 Hz), 8.15 (d, 2H, $J$=8.5 Hz).

**2.2.11. 4-Octyloxyphenyl 4′-(6-(cinnamoyloxy)hexyloxy)-4-biphenylcarboxylate (2a).** This was obtained in 70% yield from **9a** and 4-octyloxyphenol by following the procedure for **1**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.90 (t, 3H, $J$=6.9 Hz), 1.31 (m, 8H), 1.46–1.57 (m, 6H), 1.74–1.88 (m, 6H), 3.96 (t, 2H, $J$=6.5 Hz), 4.03 (t, 2H, $J$=6.4 Hz), 4.24 (t, 2H, $J$=6.6 Hz), 6.45 (d, 1H, $J$=16.0 Hz), 6.93 (d, 2H, $J$=9.0 Hz), 7.0 (d, 2H, $J$=8.8 Hz), 7.13 (d, 2H, $J$=9.0 Hz), 7.38 (m, 3H), 7.51–7.54 (m, 2H), 7.58 (d, 2H, $J$=8.8 Hz), 7.67 (d, 2H, $J$=8.5 Hz), 7.69 (d, 2H, $J$=16.0 Hz), 8.22 (d, 2H, $J$=8.5 Hz); MALDI-TOFMS ($M$+Na=671.33) $m/z$ 671.6 $[M+Na]^+$.

**2.2.12. 4-Octyloxyphenyl 4′-(2-(cinnamoyloxy)ethoxy)-4-biphenylcarboxylate (2b).** This was obtained in 66% yield from **9b** and 4-octyloxyphenol by following the procedure for **1**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.90 (t, 3H, $J$=7.0 Hz), 1.32 (m, 8H), 1.47 (m, 2H), 1.75–1.84 (m, 2H), 3.96 (t, 2H, $J$=6.6 Hz), 4.32 (t, 2H, $J$=4.8 Hz), 4.61 (t, 2H, $J$=4.8 Hz), 6.50 (d, 1H, $J$=16.1 Hz), 6.93 (d, 2H, $J$=9.0 Hz), 7.06 (d, 2H, $J$=8.8 Hz), 7.13 (d, 2H, $J$=9.0 Hz), 7.34 (m, 3H), 7.51–7.55 (m, 2H), 7.62 (d, 2H, $J$=8.8 Hz), 7.68 (d, 2H, $J$=8.5 Hz), 7.73 (d, 1H, $J$=16.1 Hz), 8.23 (d, 2H, $J$=8.5 Hz); MALDI-TOFMS ($M$+Na=615.27) $m/z$ 615.6 $[M+Na]^+$.

**2.2.13. 4-Methoxyphenyl 4′-(6-(cinnamoyloxy)hexyloxy)-4-biphenylcarboxylate (2c).** This was obtained in 49% yield from **9a** and 4-methoxyphenol by following the procedure for **1**: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.54 (m, 4H), 1.77 (m, 4H), 1.86 (m, 4H), 3.83 (s, 3H), 4.04 (t, 2H, J=6.4 Hz), 4.24 (t, 2H, $J$=6.6 Hz), 6.44 (d, 1H, $J$=16.0), 6.95 (d, 2H, $J$=9.0 Hz), 7.00 (d, 2H, $J$=8.7 Hz), 7.15 (d, 2H, $J$=9.0 Hz), 7.38 (m, 3H), 7.51–7.54 (m, 2H), 7.58 (d, 2H, $J$=8.7 Hz), 7.67 (d, 2H, $J$=8.4 Hz), 7.69 (d, 1H, $J$=16.0 Hz), 8.22 (d, 2H, $J$=8.4 Hz); MALDI-TOFMS ($M$+Na=573.22) $m/z$ 573.7 $[M+Na]^+$.

### 2.3. *Photoirradiation*

We placed 2 mg of the LC monomer with or without a triplet sensitizer (2 wt%), Michler's ketone which was

purified by recrystallization from EtOH before use, between cover glasses (Matsunami Glass Ind., Ltd, Japan) and heated it to an isotropic phase with a Linkam LK-600PH temperature controller. From the isotropic phase, the samples were cooled to the prescribed temperature (as stated in section 3) at a rate of 5°C min$^{-1}$. While the temperature was maintained at the prescribed point, the samples were irradiated with UV light. The samples with the triplet sensitizer were irradiated with monochromatic UV light at 365 nm (5 mW cm$^{-2}$) from a 500-W high-pressure mercury lamp through optical filters. As the LC monomers themselves do not have an absorption band around 365 nm ($\lambda_{max}$=274 nm in $CHCl_3$ solution), samples without the triplet sensitizer were irradiated with the high-pressure mercury lamp without any optical filters (20 mW cm$^{-2}$ at 365 nm). However, the wavelength of the light that could reach the samples was longer than 300 nm (the pass wavelength of the cover glass). During the irradiation, the samples were occasionally turned so that the total irradiation time was equal on both sides. After irradiation for a specified time, the cover glasses were carefully separated and the irradiated samples were analyzed by $^1$H nuclear magnetic resonance (NMR) spectroscopy, matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOFMS), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and X-ray diffractometry (XRD).

### 2.4. *Characterization*

The thermal properties of the samples were evaluated by polarized optical microscopy (POM) using an Olympus BH2 equipped with a Mettler FP82HT hot stage and by DSC using a Seiko Instruments Inc. DSC 6200. Heating and cooling rates were 5°C min$^{-1}$. $^1$H NMR spectra were obtained on a JEOL GSX-270 (270 MHz) or a Varian Gemini-2000/300BB (300 MHz). Mass spectrometric analysis was performed with a Voyager DE Pro (Applied Biosystems) MALDI-TOF mass spectrometer in reflection mode using 2,5-dihydroxybenzoic acid as the matrix. GPC chromatograms were recorded on a Shimadzu system (an LC-10ADvp pump unit, an SPD-10Avp UV detector, a CTO-10Avp column oven and an SCL-10Avp controller) with Shodex KF800D and KF805L columns, using THF as the eluent. X-ray diffraction patterns were measured using a Rigaku diffractometer (type 4037) with an imaging plate (R-Axis IV). The samples were placed in quartz capillary tubes (1.5 mm diameter; 0.01 mm wall thickness) and positioned on a Mettler hot stage. They were heated to their isotropic phase, cooled to the mesophase and then exposed to an X-ray beam.

## 3. Results and discussion

### 3.1. *Mesomorphic properties of the monomers*

The thermal properties of the monomers are listed in table 1. All cooling data were obtained in the first cooling process. The heating data of **1** and **2b** were recorded in the second heating process. However, the first heating data obtained from freshly recrystallized samples were used for **2a** and **2c**, because the samples did not show clear crystallization on the cooling scan, and on the subsequent heating scan they exhibited complicated thermal behaviour including a cold crystallization, which depended on the cooling and heating rates. Compound **1** showed only a nematic phase as mesophase, similar to non-cinnamoyl- and α,ω-dicinnamoyl-functionalized analogues, that is, 1,4-bis-(4-(hexyloxy)benzoyloxy)benzene (Cr 126 N 208 I (°C)) (see [21]) and 1,4-bis-(4-(6-cinnamoyloxy)hexyloxy)benzoyloxy)benzene (Cr 102 N 116 I (°C)) (the phase transition temperatures were obtained from the first heating of the sample freshly prepared by recrystallization. The phase

Table 1. Phase-transition temperatures for monomers **1** and **2a–c**.

| | Temperatures (°C) (enthalpies (kJ mol$^{-1}$)) | |
|---|---|---|
| Compound | Heating[a] | Cooling[b] |
| **1** | Cr 98 (10.4) N 161 (0.17) I | I 157 (0.17) N 54 (4.7) Cr |
| **2a** | Cr 93 (10.0) SmA 146 (0.66) N 152 (0.29) I | I 149 (0.26) N 144 (0.60) SmA 93 (—)[c] SmC 77 (0.29) SmX 74 (0.21) SmX 63 (0.64) SmX 38 (1.26) SmX |
| **2b** | Cr 119 (9.0) SmA 125 (0.09) N 132 (0.10) I | I 130 (0.13) N 123 (0.21) SmA 107 (—)[c] SmC 105 (10.1) Cr |
| **2c** | Cr 125 (12.4) SmA 135 (0.25) N 163 (0.09) I | I 161 (0.10) N 133 (0.42) SmA 92 (0.68) SmX 73 (0.66) SmX |

[a]Determined by DSC and POM on first heating for **2a** and **2c** and on second heating for **1** and **2b**. [b]Determined by DSC and POM on first cooling. [c]Not detected by DSC. Cr=crystalline phase; N=nematic phase; SmA=smectic A phase; SmC=smectic C phase; SmX=unidentified smectic phase; I=isotropic phase.

transition temperatures of the first cooling process are reported in [14]). The clearing point of **1** (161°C) lay between those of the analogues. Monomers **2a–c** exhibited not only a nematic phase, but also a smectic A phase, as might be expected of a phenyl biphenyl-4-carboxylate mesogen. It is also a general tendency that the nematic-phase temperature range of **2c**, which has a short terminal alkyl chain, is wider than those of **2a** and **2b**, which possess a longer terminal alkyl chain.

### 3.2. *Photoirradiation of 1*

In a previous study [14], we could easily confirm the generation of the higher-molecular-weight compounds on the photoirradiation of the bifunctional monomer by means of GPC measurement. Therefore, in the present study, first we performed GPC analysis of **1** after UV irradiation. The samples of **1** with and without the triplet sensitizer were irradiated with UV light at 365 nm and with UV light above 300 nm, respectively, in the nematic phase at 130°C for a prescribed period of time and then dissolved in THF for GPC analysis. The GPC results are shown in figure 1. Even without the sensitizer, the formation of a compound whose molecular weight was higher than that of **1** was confirmed; however, its rate of increase was very low. In contrast, from the sample containing the sensitizer, a higher-molecular-weight compound was formed rapidly and it is noteworthy that almost all of monomer **1** was consumed at least in 30 min, although the intensity of light at 365 nm was smaller than that used in the UV irradiation of the samples without the sensitizer. MALDI-TOFMS showed that the higher-molecular-weight compound had a molecular mass of 1329.57 and was thus a dimer of **1**. The nematic phase of the sample with the sensitizer was maintained during UV irradiation for 30 min, as indicated by POM. A small shoulder associated with a compound with a higher molecular weight than that of the dimer was seen in the GPC chromatograms. We think that this compound was derived from the dimer through an unnecessary photochemical reaction; however, its chemical structure has not been identified yet because it cannot be detected by $^1$H NMR or MALDI-TOFMS.

$^1$H NMR spectra of **1** recorded before and after UV irradiation in the presence of the sensitizer for 30 min are shown in figure 2. The two doublet proton peaks associated with a double bond of a cinnamoyl group, which were seen at 6.45 and 7.69 ppm before UV irradiation, completely disappeared after UV irradiation. Instead, new peaks corresponding to a cyclobutane were observed at around 3.4–4.4 ppm after UV irradiation. According to the literature [12, 13, 22, 23], the chemical sift and the pattern of the dominant peaks at 3.48 and 3.75 ppm indicate that the cyclobutane unit obtained tends to have a $\delta$-type structure, that is, an *anti*-head-to-head configuration. We conclude that energy was efficiently transferred from triplet-excited Michler's ketone to a cinnamoyl group of **1**, then the excited cinnamoyl group underwent [2+2] cycloaddition, as shown in scheme 4. The reaction mixture containing **1** and the dimer preserved the nematic phase no matter what composition the reaction mixture had. While it is

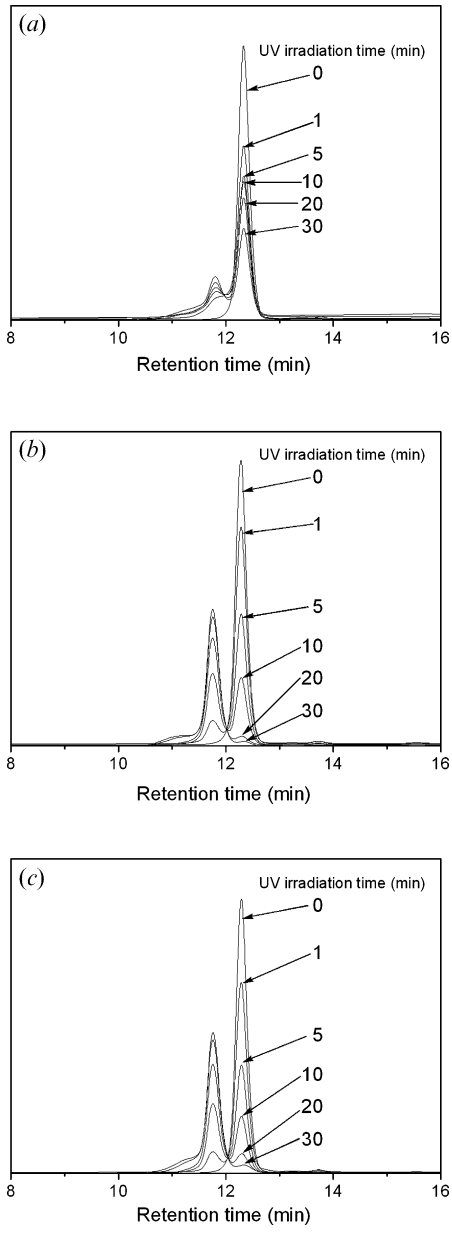



Figure 1. GPC charts of **1**: (a) without Michler's ketone irradiated with UV light (>300 nm) at 130°C; and with Michler's ketone irradiated with UV light (365 nm) at (b) 130 and (c) 180°C for various lengths of time.

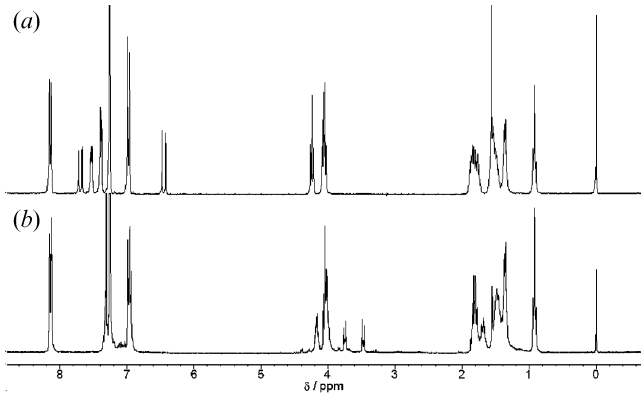
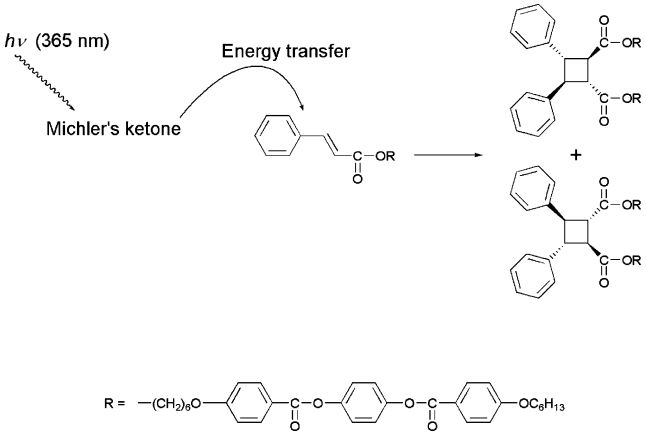



Figure 2. $^1$H NMR spectra of (a) pure compound **1** and (b) **1** containing Michler's ketone irradiated with UV light (365 nm) for 30 min.




Scheme 4. Route of synthesis of the LC dimer derived from **1** through energy transfer from the triplet sensitizer.

possible that $\delta$-truxinate could have enantiomers, the racemic compound was produced by UV irradiation of **1**, as confirmed by the fact that the dimer showed no chiral LC phases.

In our previous study [14], the photochemical conversion from the bifunctional monomer, 1,4-bis-(4-(6-cinnamoyloxy)hexyloxy)benzoyloxy)benzene, to the oligomer could not exceed 84% even after 120 min of irradiation in the presence of the sensitizer. Moreover, we observed not only the resulting cyclobutane unit, but also unreacted and *cis*-isomerized cinnamoyl groups in the $^1$H NMR spectrum of the irradiated sample. In contrast here, all of the cinnamoyl group of **1** was consumed after 30 min of irradiation and the photochemical conversion from **1** to the dimer could be regarded as 100%. This is probably due to the high mobility of the dimer obtained from **1**, which did not result in an increase in the viscosity of the reaction mixture. In contrast, as the length of the oligomers obtained from the difunctional monomer increased, the viscosity of the reaction mixture and the distance between the ends of the oligomers increased. Therefore, the probability of collision between two excited cinnamoyl groups decreased, resulting in the relatively low conversion efficiency.

Figure 3 compares the DSC curve of **1** obtained after UV irradiation for 30 min in the presence of the sensitizer with that obtained from a pure compound of **1**. Whereas the irradiated sample of **1** had a bulky cyclobutane with two phenyl rings, it showed a clearing point at 165°C, which was 8°C higher than that of pure **1**. In addition, the irradiated sample exhibited a smectic C phase, which was not observed in **1** before irradiation. The smectic C phase was confirmed by a Schlieren texture observed by POM and the detection of diffraction associated with a smectic layer by XRD at a temperature below that of phase transition. Such thermal properties were obviously due to the effect of dimerization.

To investigate effects of the LC phase on the dimerization reaction, we UV-irradiated **1** in the presence of the sensitizer in the isotropic phase at 180°C. GPC curves of samples irradiated for various lengths of time at 180°C are depicted in figure 1 (c). There is no significant difference from the GPC result obtained from UV irradiation in the nematic phase at 130°C (figure 1 (b)), which means that the dimerization reaction rate was not affected by the environmental phase. We also carried out $^1$H NMR measurement of **1** irradiated with UV light for 30 min at 180°C. As seen in the sample irradiated in the nematic phase, the cyclobutane unit resulting from the dimerization predominantly had an *anti*-head-to-head structure. Diethyl $\delta$-truxinate, which has an *anti*-head-to-head structure, dominantly formed when the isotropic melt of an ethyl

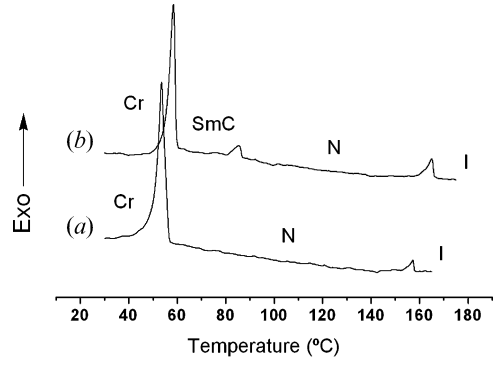



Figure 3. DSC thermograms of (a) pure compound **1** and (b) **1** containing Michler's ketone irradiated with UV light (365 nm) for 30 min, recorded on the first cooling.

cinnamate was irradiated with UV light [24]. It is also mentioned that steric factors of the ester group must play a role in determining the cyclobutane structure [24]. From these facts, we can conclude that the LC phase has the ability neither to accelerate the photodimerization nor to impart a topochemical environment.

It is well known that photodimerization of a cinnamic acid in the crystalline phase is based on topochemical principles [25]. We previously found that photopolymerization of the dicinnamoyl-functionalized LC monomer in the crystalline state also proceeded topochemically [26]. Our study of the photodimerization of monocinnamoyl-functionalized LC monomers in the crystalline state will be reported elsewhere.

### 3.3. *Photoirradiation of 2a–c*

As the dimer obtained by photoirradiation of **1** showed the LC phase, it seems plausible that the two mesogens in the dimer lie parallel to each other and occur on either the same side or the opposite side relative to the cyclobutane in the LC phase, as schematically illustrated in figure 4. Elucidation of this point was one of the reasons why we UV-irradiated **2a–c** in the presence of the triplet sensitizer. **2a**, **2b** and **2c** were irradiated in the LC phases at 130, 120 and 140°C, respectively. As seen in the photodimerization of **1**, most of each sample was converted into the respective dimers after at least 30 min and the resulting cyclobutane units dominantly had a $\delta$-type structure, as confirmed by GPC and $^1$H NMR measurements. All of the samples of **2a–c** maintained their LC phases during UV irradiation.

The samples obtained by UV irradiation of **2a**, **2b** and **2c** for 30 min are designated as **10a**, **10b** and **10c**, respectively. Their chemical structures and thermal properties determined by DSC and POM analyses are shown in scheme 5 and table 2, respectively. While **10b** showed a monotropic LC phase, **10a** and **10c** exhibited enantiotropic LC phases. Dimers **10a** and **10c** did not

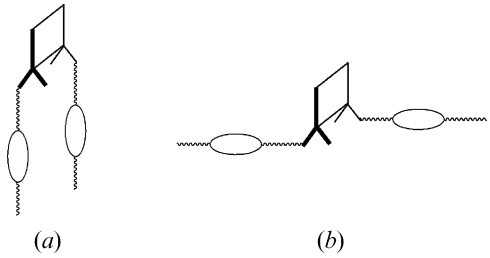
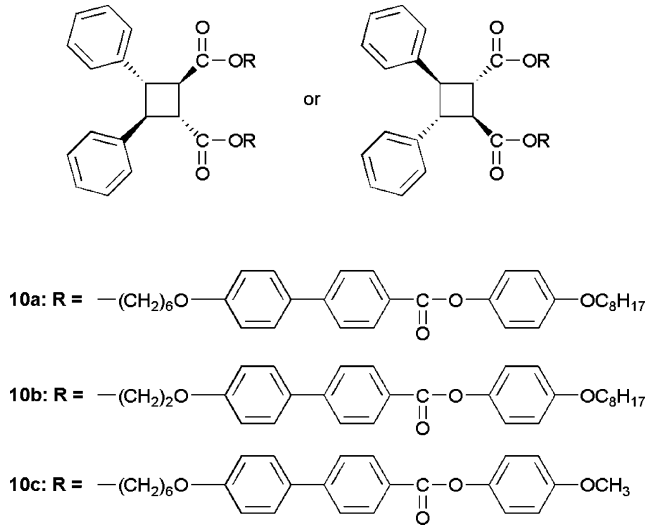



Figure 4. Schematic illustration of plausible conformations of the LC dimer derived from **1**. The mesogens occur on either (a) the same side or (b) the opposite side relative to the cyclobutane.




Scheme 5. The chemical structures of dimers **10a–c**.

show crystallization on the cooling scans or cold crystallization on the heating scans, which we attributed to glass transition. We could not determine a crystallization temperature or an enthalpy of transition of **10b** during cooling, because the crystallization rate was very slow, whereas a crystalline-to-isotropic transition was clearly detected at 178°C, accompanied by a large enthalpy on heating scan. All of the clearing points of the dimers shifted to higher temperatures than those of the monomer; in particular, the isotropic-to-smectic-A transition temperature of **10b** was 37°C higher than that of **2b**. The nematic-phase temperature range of **2c** decreased from 28 to 4°C, and those of monomers **2a** and **2b** disappeared with UV irradiation, while the thermal stability of the smectic phases increased, owing to dimerization.

As all of the monomers **2a–c** and the corresponding dimers showed smectic A phases, we investigated smectic layer distances ($d$) with XRD. The results are listed in table 3. The molecular lengths of the all-*trans* conformation of the monomers ($L$) determined by molecular modelling are also shown in table 3. The values of $L$ are almost consistent with those of $d$ and it is reasonable that the former are somewhat larger than the latter, as was the case for **2a** and **2b**, which have long terminal alkyl groups. We must note that the $d$ values of all of the dimers are almost the same as those of the corresponding monomers. Also, we performed XRD measurement of the dimers of samples that had been heated to the isotropic phase and subsequently cooled to the smectic A phase, which means that the estimated $d$ values are intrinsic to the dimers.

If the dimer had a conformation such as that shown in figure 4 (b) and the mesogens do not intercalate in the

Table 2. Phase-transition temperatures for dimers **10a–c**.

| Compound | Temperatures (°C) (enthalpies (kJ mol$^{-1}$)) | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Heating[a] | | | | | | | | | Cooling[b] | | | | | | | | | |
| **10a** | SmX | 113 (0.55) | SmA | 167 (1.92) | I | | | | | I | 162 (1.79) | SmA | 105 (0.69) | SmX | | | | | |
| **10b** | Cr | 178 (8.94) | I | | | | | | | I | 167 (1.58) | SmA | | | | | | | |
| **10c** | SmX | 89 (0.75) | SmX | 101 (0.57) | SmA | 179 (—)[c] | N | 184 (2.17) | I | I | 183 (1.59) | N | 179 (—)[c] | SmA | 97 (0.66) | SmX | 83 (0.79) | SmX | |

[a]Determined by DSC and POM on second heating. [b]Determined by DSC and POM on first cooling. [c]Overlapped with the isotropization peak Cr=crystalline phase; N=nematic phase; SmA=smectic A phase; SmC=smectic C phase; SmX=unidentified smectic phase; I=isotropic phase.

Table 3. Smectic layer distances and molecular lengths for monomers **2a–c** and dimers **10a–c**.

| Compound | Smectic layer distance[a] $d$ (nm) | Molecular length[b] $L$ (nm) |
|---|---|---|
| **2a** | 3.97 | 4.29 |
| **2b** | 3.42 | 3.41 |
| **2c** | 3.51 | 3.78 |
| **10a** | 3.98 | |
| **10b** | 3.42 | |
| **10c** | 3.59 | |

[a]Determined by XRD in the smectic A phase. [b]Measured from molecular modelling of fully extended chains.



smectic A phase, the $d$ value should have been around $2L$. In the case of dimer **10a**, because the spacer is about twice the length of the terminal alkyl chain, an intercalated smectic A phase can be drawn, as shown in figure 5. Therefore, the $d$ value is similar to that of $L$. However, an intercalated arrangement cannot be adopted for **10b** and **10c**, because the differences in the lengths between the spacers and the alkyl terminal chains are too large. Furthermore, it is rare for LC dimers that possess identical mesogens to have an intercalated structure [16]. Consequently, we consider the LC dimers to have a conformation in which the two mesogens align laterally and exist in the same smectic layer, so the $d$ spacing becomes similar to the $L$ value, as shown in figure 6.

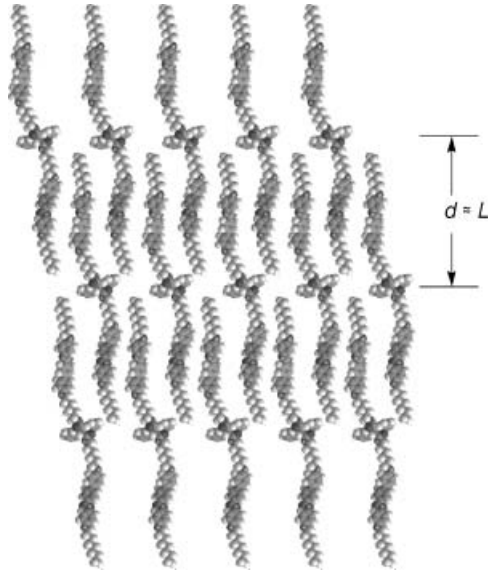



Figure 5. Possible molecular organization of an intercalated smectic A phase, which can be drawn if **10a** has a conformation in which two mesogens appear on the opposite side relative to the cyclobutane.

## 4. Conclusion

LC monomers having a cinnamoyl moiety on their extremity have been irradiated with UV light in their LC phase. In the presence of a triplet sensitizer, most were converted into the corresponding LC dimers through the cycloaddition reaction of the cinnamoyl group. Although the LC dimers had a bulky cyclobutane with two phenyl rings, their LC phases were not significantly different from those of the corresponding LC monomers and were more thermally stable. Therefore, UV irradiation can cause isothermal phase transitions, such as nematic-to-smectic and isotropic-to-nematic transitions, of the monomers. The cyclobutane unit of the dimers predominantly had an *anti*-head-to-head structure. This was also the case for the dimers obtained by UV irradiation of the monomers in their isotropic phase, which suggests that the LC phase could not present a topochemical reaction field to the cinnamoyl group. XRD studies of the smectic LC monomers and the corresponding LC dimers with various lengths of spacers and terminal alkyl chains revealed that the two mesogens of the dimers existed on the same side relative to the cyclobutane unit in their LC phases. If this is the case for the main-chain LC

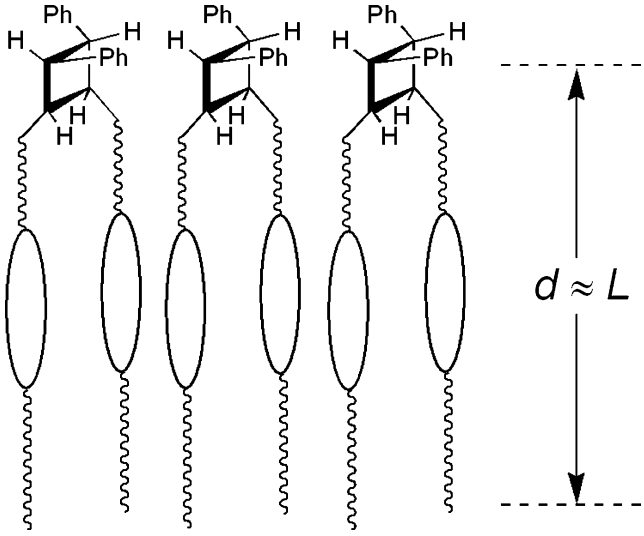



Figure 6. Schematic illustration for the conformation of the LC dimers determined by consideration based on XRD analysis of **10a–c**.

oligomer, which was previously prepared from the dicinnamoyl-functionalized LC monomer, then the oligomer has a structure in which the mesogens are connected in a folding manner rather than a straight manner. Like this inference, further studies of *in situ* photochemical conversion from LC monomers to LC dimers will give us profound insights into not only the mechanism of the cycloaddition reaction of cinnamoyl groups, but also the photopolymerization of LC polymers.

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