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Modification of the pitch of chiral nematic liquid crystals by means of photoisomerization of chiral dopants

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New photoisomerizable chiral dopants have been studied. The dopants used were menthone derivatives, a chiral stilbene derivative and a nematic copolymer of a menthone derivative and a benzoyloxybenzonitrile derivative. NMR, HPLC and UV results showed that the *E–Z*-isomerization of all the compounds indicated proceeded rapidly upon UV exposure, without the formation of undesired by-products. Isomerization of the menthone derivatives, including the copolymer, induced a substantial decrease in the helical twisting power. The changes in helical twisting power induced by the isomerization of the chiral stilbene derivative were limited to a factor of 2. In mixtures of the photoisomerizable dopants with commercial dopants of opposite twisting senses and a nematic host mixture, the sign of the twisting sense could be reversed by illuminating the mixture with UV light. The viewing angle dependence of irradiated regions of a 90°-twisted nematic cell was rotated 90° with respect to the viewing angle dependence of the non-irradiated regions. It is expected that this approach may be useful in the preparation of dual domain TN cells with a reduced viewing angle dependence.

1. Introduction

Photochemical modulation of the properties of liquid crystals has received much attention over the past few years. The ability to adjust specific properties of liquid crystals with the aid of an external light source raises many intriguing possibilities. For instance, much research has been devoted to the photochemical manipulation of orientation layers for liquid crystals (see, for instance, references [1–3]). The photochemical modification of the spontaneous polarization of ferroelectric liquid crystals has received some interest [4–6]. Properties that can be photochemically addressed will also have a potential for optical recording [7–11].

The influence of photochemical processes on the properties of chiral nematic liquid crystals has scarcely been studied. Photodegradation of chiral groups has been used to manipulate the reflection wavelength of cholesteric liquid crystals [12–14]. Feringa *et al.* [15] and Zhang and Schuster [16] developed special photochemical isomerization reactions to influence the chirality of compounds. Yarmolenko *et al.* studied the influence of photoisomerization processes on the pitch of chiral menthone derivatives dissolved in liquid crystals [17].

Here we would like to discuss changes in twisting power due to isomerization reactions in more detail and to use the principle to manipulate the twist sense of liquid crystals in liquid crystal displays. The ability to control the twist sense of twisted nematic displays in microscopic domains is a useful tool for extending the viewing angle of TN cells [18–20].

The materials used in the experiments were a chiral stilbene derivative and menthone derivatives (see figure 1). The properties of a nematic copolymer containing a photoisomerizable chiral group and a non-photoisomerizable group will also be described.

2. Experimental

2.1. *Materials*

E7, ZLI 4792, S811 and R811 were obtained from E. Merck (Darmstadt, Germany). All the solvents were also obtained from E. Merck. Irgacure 651 was obtained from Ciba Geigy (Switzerland). All the other chemicals were obtained from Aldrich. The following chemicals were prepared according to procedures described in the literature: 4-(6-acryloyloxyhexyloxy)benzoic acid [21], 4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzonitrile [22].

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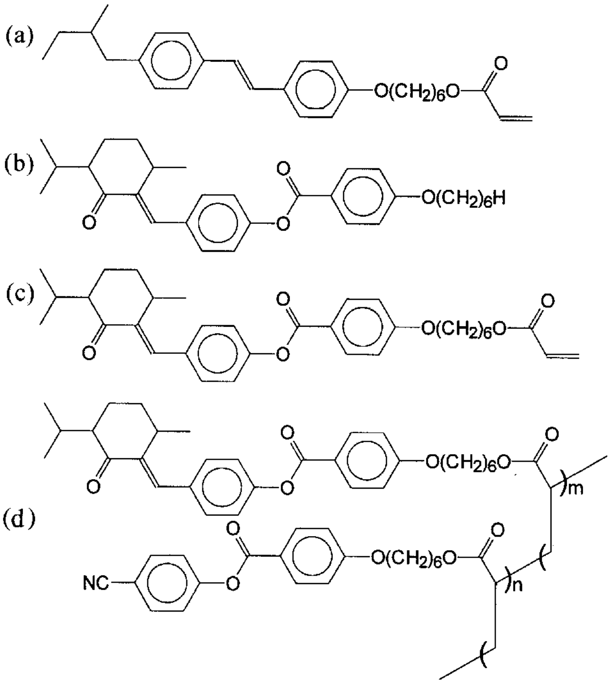
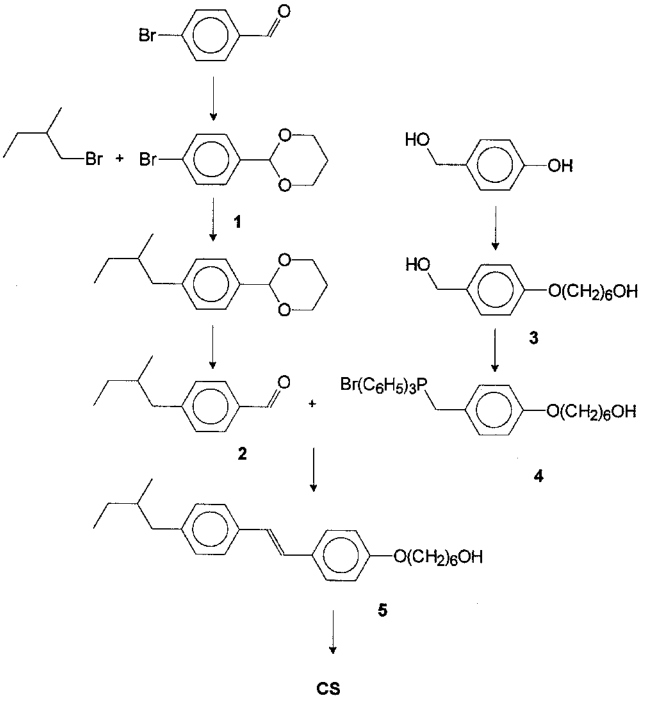


Figure 1. Structural formulae of the compounds: (*a*) chiral stilbene derivative (**CS**); (*b*) non-reactive menthone derivative (**NRM**); (*c*) reactive menthone derivative (**RM**); (*d*) random copolymer of cyano-monoacrylate (**CN6**) and **RM** (16 mol % **RM**, 84 mol % **CN6**).

2.2. *Synthesis*

2.2.1. *Synthesis of chiral stilbene **CS** (see scheme 1)*



Scheme 1. Synthetic scheme showing the preparation of the chiral stilbene derivative.

2.2.1.1. *2-(4-Bromophenyl) 1,3-dioxane (**1**).* A mixture of 100 g of 4-bromobenzaldehyde, 0·6 g of 4-toluenesulphonic acid, 45 ml of 1,3-propanediol and 200 ml of toluene was heated at reflux for 3 h with constant removal of water (Dean and Stark apparatus). After cooling, a solution of 1·5 g of potassium hydroxide in 15 ml of ethanol was added and the mixture was stirred for 10 min. After washing the toluene layer with 100 ml of water and then with 100 ml of brine, the toluene solution was dried over magnesium sulphate and evaporated. The crude residue was recrystallized from a mixture of 400 ml of ethanol and 100 ml of water. Compound **1** was obtained as white plates (yield: 99 g, 81%).

2.2.1.2. *(S)-4-(2-Methylbutyl) benzaldehyde (**2**).* A solution of the Grignard reagent of 2-(4-bromophenyl) 1,3-dioxane in 200 ml of tetrahydrofuran was prepared from 2·5 g of magnesium and 16 g of 2-(4-bromophenyl) 1,3-dioxane (**1**). After filtration, 0·5 g of copper(I) chloride and 10 g of (*S*)-1-bromo-2-methylbutane were added. This mixture was heated at reflux for 16 h. After the addition of 50 ml of 2·5 M aqueous HCl, the mixture was stirred for one day at room temperature. The organic layer was separated and the aqueous layer shaken twice with 50 ml of diethyl ether. The combined organic layers were subsequently washed with 75 ml of a saturated sodium bicarbonate solution and 75 ml of brine. After drying over magnesium sulphate and evaporation, a brown oil was obtained which was fractionated (b.p. = 72–74°C at 0·4 mbar) to yield 4·4 g of compound **2** as a clear oil (yield 38%).

2.2.1.3. *4-Hydroxymethyl-(6-hydroxyhexyloxy) benzene (**3**).* A mixture of 55 g of 6-chlorohexanol, 66 g of sodium iodide and 250 ml of butanone was heated at reflux for 8 h. After cooling, the salts were filtered off and 56 g of 4-hydroxybenzylalcohol and 83 g of potassium carbonate were added. After boiling for 24 h, the butanone was evaporated and 300 ml of ethyl acetate and 300 ml of 5% aqueous sodium hydroxide were added to the residue. After separation, the organic layer was successively washed with 300 ml of 5% aqueous sodium hydroxide and 200 ml of brine. After drying over magnesium sulphate and evaporation of the ethyl acetate, a solid was obtained which was recrystallized from 250 ml of toluene. Compound **3** was obtained as a white powder (56 g, 62% yield).

2.2.1.4. *4-(6-Hydroxyhexyloxy) phenylmethyltriphenylphosphonium bromide (**4**).* A mixture of 10 g of 4-hydroxymethyl-(6-hydroxyhexyloxy)benzene (**3**), 15·3 g of triphenylphosphonium bromide and 50 ml of dichloromethane was vigorously stirred for 2 h after which a clear solution was obtained. After the addition of 50 ml of toluene and cooling to 0°C, the product separated as a white powder, which was collected and dried at 60°C in a vacuum. Compound **4** (21·5 g) was obtained in a yield of 88%.

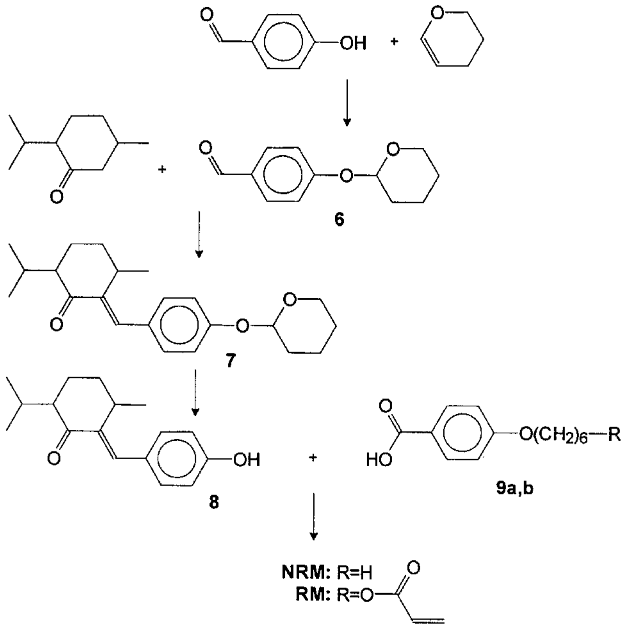
2.2.1.5. *(E)-(S)-4-(2-Methylbutyl)-4′-(6-hydroxyhexyloxy)-stilbene (**5**).* 0·2 g of lithium was added to 75 ml of ethanol. After complete dissolution, 4·4 g of (*S*)-4-(2-methylbutyl)-benzaldehyde (**2**) was added. The solution was cooled in an ice bath and 13·7 g of 4-(6-hydroxyhexyloxy)-phenylmethyltriphenylphosphonium bromide (**4**) was added. After stirring for 1 h, 1 ml of acetic acid was added and the mixture left in a refrigerator (−20°C) overnight. The precipitated crude product was recrystallized from 250 ml of methanol at (−20°C). Compound **5** (1·6 g) was obtained as a waxy solid (yield 17%).

2.2.1.6. *(E)-(S)-4-(2-Methylbutyl)-4′-(6-acryloyloxy-hexyloxy)stilbene (**CS**).* A mixture of 1·6 g of (*E*)-(*S*)-4-(2-methylbutyl)-4′-(6-hydroxyhexyloxy)stilbene (**5**), 0·6 ml of *N*,*N*-dimethylaniline and 25 ml of dichloromethane was cooled in an ice bath. 0·4 ml of acryloyl chloride was added, after which the ice bath was removed. After stirring for one night at room temperature, 20 ml of 2·5 M aqueous HCl was added. After separation, the dichloromethane layer was washed with 10 ml of brine, dried over magnesium sulphate and evaporated. **CS** was obtained as a white powder (1·1 g) after recrystallization from 20 ml of hexane (yield 62%).

2.2.2. *Synthesis of non-reactive (NRM) and reactive (RM) menthanes (see scheme 2)*

2.2.2.1. *4-(Tetrahydropyran-2-yloxy)benzaldehyde (**6**).* To a solution of 30 g of 4-hydroxybenzaldehyde and 3 g of pyridinium 4-toluenesulphonate in 200 ml of dichloromethane, cooled in an ice bath, 28 ml of 2,3-dihydropyran was added drop by drop. After the addition, the ice bath was removed and the solution stirred for one day at room temperature. The solution was washed successively with 100 ml of half-saturated brine, 100 ml of 5% aqueous sodium hydroxide and 100 ml of brine. After drying over magnesium sulphate, the dichloromethane and the excess of 2,3-dihydropyran were evaporated. Compound **6** (47 g) was obtained as a clear oil (yield 93%).

2.2.2.2. *(1R,4R)-2-(Hydroxybenzylidene)menth-3-one, mixture of the E and Z isomers (**8**).* Powdered potassium hydroxide (1·8 g) was stirred for 10 min with 25 ml of dimethyl sulphoxide. Then 33·4 g of 4-(tetrahydropyran-2-yloxy)benzaldehyde (**6**) and 25 g of menthone were added. After stirring for one day at room temperature, 200 ml of diethyl ether were added. This solution was washed three times with 100 ml of 2·5 M aqueous HCl and once with 100 ml of brine. After evaporation, a brown paste was obtained which was dissolved in 200 ml of ethanol together with 4 g of pyridinium 4-toluenesulphonate. This mixture was heated to 50°C for 4 h. After cooling, 200 ml of diethyl ether was added and the mixture was washed four times with 100 ml of brine. After drying over magnesium sulphate and evaporation, a brown paste was obtained which was eluted twice over silica with a solution of 4% diethyl ether in dichloromethane. The solid obtained was washed with 60 ml of pentane. Compound **8** (9·3 g) was obtained as a white powder (yield 22%).



Scheme 2. Synthetic scheme showing the preparation of the reactive menthone (**RM**) derivative and the non-reactive menthone (**NRM**) derivative.

2.2.2.3. *(E)-(1R,4R)-2-[4-(hexyloxybenzoyloxy)benzylidene]menth-3-one (**NRM**).* A mixture of 3·2 g of (1*R*,4*R*)-2-(4-hydroxybenzylidene)menth-3-one (**8**), 2·7 g of 4-hexyloxybenzoic acid, 0·15 g of 4-*N*,*N*-dimethylaminopyridine and 35 ml of dichloromethane was cooled in an ice bath. *N*,*N*′-dicyclohexylcarbodiimide (2·8 g) was added and the mixture was allowed to stir for 1 h while being cooled in the ice bath. After removal of the ice bath, the stirring was continued for one day at room temperature. The crude product obtained after filtration through a layer of silica and evaporation of the dichloromethane, was recrystallized twice from 35 ml of ethanol. The product **NRM** (3·6 g) was obtained as white needles (yield: 64%).

2.2.2.4. *(E)-(1R,4R)-2-{4-[4-(6-acryloyloxyhexyloxy)-benzoyloxy]benzylidene}menth-3-one (**RM**)*. This compound was prepared in 57% yield in a similar way to **NRM**, except that 4-hexyloxybenzoic acid was replaced by 4-(6-acryloyloxyhexyloxy)benzoic acid.

2.2.3. *Synthesis of the copolymer poly{[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzonitrile-co-(E)-(1R,4R)-2-[4-(4-(6-acryloyloxyhexyloxy)-benzoyloxy)benzylidene]menth-3-one}*

A solution of 2·0 g of 4-[4-(6-acryloyloxyhexyloxy)-benzoyloxy]benzonitrile, 0·5 g of (*E*)-(1*R*,4*R*)-2-[4-(4-(6-acryloyloxyhexyloxy)benzoyloxy)benzylidene]menth-3-one (**RM**), 20 mg of azoisobutyronitrile and 70 mg of *n*-decanethiol in 25 ml of toluene was deaerated in three freeze-thaw cycles. The polymerization was allowed to proceed for 24 h at 60°C. The polymer was precipitated in 100 ml of cold diethyl ether and separated by centrifugation. After a second precipitation step it was dried at 60°C in a vacuum. Yield: 820 mg, 33%.

2.3. *Methods*

The irradiations were performed using a 500 W Hg light source (Philips SP500). The intensities were measured using an IL1700 photodetector and a WBS 320 filter (IL, Newburyport, MA, USA). In the UV and HPLC experiments the cuvettes were covered with a 1 mm thick glass plate to cut out the deep UV irradiation (cut-off wavelength ~300 nm). This made it easier to compare the UV, HPLC and pitch measurements. The total UV intensity of the light source after it had passed the glass plate was 8 mW cm^{-2}. Phase transitions were determined using a Perkin Elmer DSC7 (heating rate 20°C min^{-1}). To study photopolymerization, we combined the DSC and a UV light source (PL10 lamp, intensity 8 mW cm^{-2}). Compositional analysis was performed using HPLC (RP18 column, gradient of acetonitrile in water, flow 1 ml min^{-1}). Molecular masses were determined relative to polystyrene standards using GPC (THF, PLgel columns). UV spectra were recorded (solutions in dichloromethane and acetonitrile) using a Unicam 8700 UV/VIS spectrophotometer. Wedge cells ($\tan \alpha = 0{\cdot}0083$) were obtained from E.H.C. Ltd (Japan); care had to be taken to equilibrate the samples after UV irradiation. Twisted nematic cells were obtained by coating ITO-covered glass with an alignment layer (AL1051, JSR, Japan), rubbing the alignment layer with a velvet cloth, coating spacers (4·3 μm, Shinshikyu, Japan) and gluing the two glass plates together at a 90° angle between the rubbing directions.

3. Results and discussion

3.1. *Synthesis*

Apart from the twist, photoisomerizable additives should not influence the other electro-optical properties of TN LC mixtures. For that reason materials with a relatively high helical twisting power should be used so that only small amounts are necessary to obtain the desired 90° twist. **CS** was thought to have such a tight pitch because similar compounds with the 2-methylbutyl group have been shown to have rather short pitches compared with those of the more easily prepared derivatives with the 2-methylbutyloxy group [23].

All products that were synthesized exhibited ^{1}H NMR spectra in accordance with their structures. The synthesis of **CS** is outlined in scheme 1. The stilbene unit was formed in a Wittig reaction between chiral aldehyde **2** and phosphonium salt **4**. The pure *E*-isomer was obtained through crystallization; it was subsequently acrylated to form **CS**. Chiral aldehyde **2** was obtained by coupling of 2-methylbutyl bromide and 4-bromobenzaldehyde, which was protected as its 1,3-dioxane derivative **1**. The phosphonium compound **4** was prepared in a straightforward manner, starting from 4-hydroxybenzyl alcohol which was alkylated by 6-chlorohexanol to form diol **3**, followed by reaction with triphenyl phosphonium bromide. In the last reaction use was made of the great difference in reactivity between the benzylic alcohol function and tiphenyl phosphonium bromide compared with the other alcoholic function.

Yarmolenko *et al.* [17] demonstrated pitch variation by irradiating the condensation product of menthone and biphenylaldehyde in a liquid crystalline mixture. Because this compound showed a high twisting power, we also included this system in our experiments. In order to obtain such a menthone derivative with an acrylate group, we decided to prepare the condensation product of menthone and 4-hydroxybenzaldehyde, **8**. This product can be derivatized to form several products containing the photoisomerizable unit. Unfortunately, we did not succeed in the condensation of menthone and 4-hydroxybenzaldehyde due to the relative acidity of the phenolic group. For that reason, compound **8** was prepared from its protected form **7**, which was in turn prepared through condensation of menthone and the protected form of 4-hydroxybenzaldehyde, **6**. Compound **8** was obtained as an 80–20 mixture of the *E*- and *Z*-isomers, which turned out to be difficult to separate. After the formation of **NRM** and **RM**, the pure *E* forms were easily obtained by crystallization. Although the purification of **8** was rather laborious, the synthesis of **NRM** is easier than that of **CS**.

As a comonomer in the polymerization of **RM**, we chose 4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzonitrile because this monomer forms nematic polymers upon polymerization [22], and it was expected that such a nematic polymer will be readily soluble in nematic liquid crystal mixtures. For the same reason, the molecular mass of the polymer was kept relatively low by performing the radical polymerization in the presence of decanethiol as a chain-transfer reagent. ^{1}H NMR analysis of the copolymer showed it to have the same composition of repeating units as the monomer feed stock (16 mol % of chiral units).

3.2. *Properties of the compounds*

The melting points of **NRM** and **RM** were 96 and 76°C, respectively. No liquid crystalline transitions were detected for these compounds. The chiral stilbene derivative **CS** showed a melting point at 71°C and a monotropic smectic to isotropic phase transition at 64°C. The copolymer showed a glass transition of 27°C and a nematic to isotropic phase transition at 103°C (figure 2). Because of the presence of 16% of non-mesogenic repeat units, the nematic to isotropic phase transition took place at a slightly lower temperature than that measured for the homopolymer of **CN6** (110°C). The molecular mass (M_n) of the copolymer was 5900 g mol^{-1} and the polydispersity was 1·3.

3.3. *Sensitivity of the reactive monomers to UV induced polymerization*

Care has to be taken in UV irradiation experiments involving monomers with acrylate groups: polymerization of the compounds is not unlikely. The sensitivity of the monomers used in our experiments to UV radiation was investigated using a DSC combined with a UV light source. A 10 wt % solution of **RM** or **CS** in ZLI 4792 was subjected to UV irradiation (figure 3). The sudden shifts in heat flow at the arrows in figure 3 are due to heat effects associated with thermal effects from the lamp. No heat effects induced by photopolymerization were observed in the DSC traces. When 2 wt % of photoinitiator was added to the solution an exothermal peak was obtained. The polymerization seemed to be largely completed within 2 min. The similarity of the results of the photoisomerization (UV spectra and pitch) of **NRM** and **RM** and the copolymer indicates that the effect of photopolymerization on the results presented here is negligible (see later sections). Furthermore, no evidence of polymerization reactions was obtained from the HPLC analysis of UV irradiated solutions. These results indicate that when no initiator is present photopolymerization is not interfering with the isomerization.

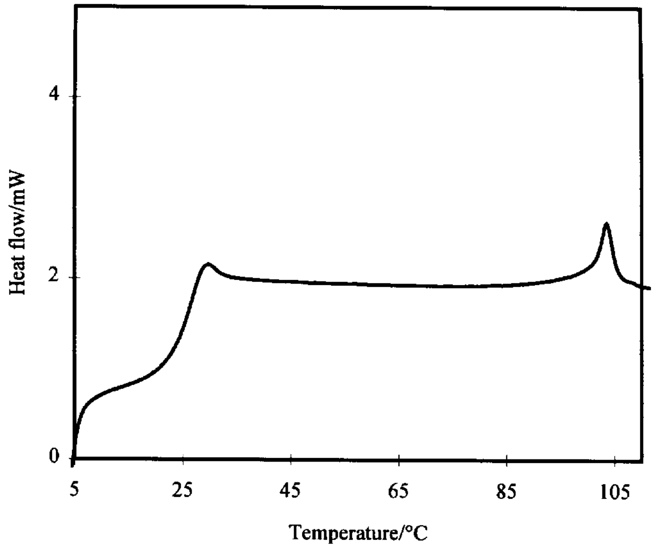


Figure 2. DSC trace of the copolymer of **RM** and **CN6**. The glass transition and the nematic to isotropic transition are clearly visible.

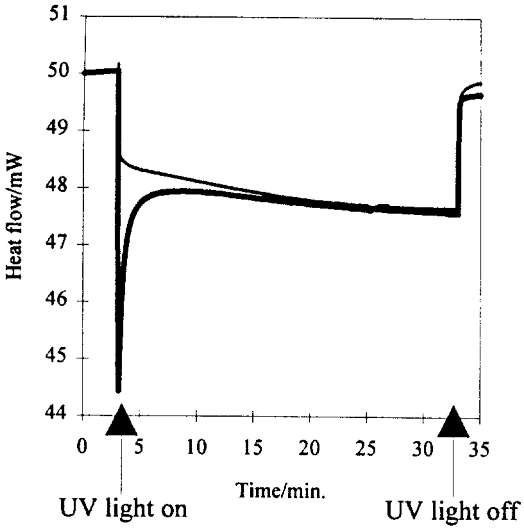


Figure 3. DSC trace of a 10 wt % solution of **CS** in ZLI 4792. The sample was subjected to UV irradiation. Thin line: no initiator added to the solution; thick line: 2 wt % Irgacure 651.

3.4. *E–Z-isomerization of the compounds: HPLC and NMR analysis*

In order to find out whether the photochemistry resulted in the expected *E–Z*-isomerizations, we recorded ^{1}H NMR spectra of solutions of **CS** and **NRM** in deuteriated dichloromethane after different irradiation times. In the case of **CS**, the signals attributable to the vinylic protons in the stilbene moiety, observed as two doublets at 6·89 and 6·96 ppm (relative to TMS), decreased in intensity upon irradiation while a new singlet appeared at 6·40 ppm. This last signal is typical of the *Z*-isomer. Subtraction of the spectrum of **CS** from the spectrum of an irradiated sample of **CS** resulted in the spectrum of the *Z*-isomer without appreciable amounts of other products. Therefore photoisomerization was indeed the main process in these experiments. The degree of conversion in the NMR tube could be determined with the aid of the two NMR signals. After prolonged irradiation a photostationary state containing 75% of the *Z*-isomer was obtained.

In the case of **NRM** the isomerization could be followed with the aid of the vinylic protons observed at 6·97 ppm in the case of the *E*-isomer and at 6·24 ppm in the case of the *Z*-isomer. In this case, too, photoisomerization turned out to be the main process. With the aid of both NMR signals, a photostationary state containing 85% of the *Z*-isomer was observed.

Using HPLC, we analysed irradiated solutions of the compounds in acetonitrile. Figure 4 clearly shows that the *E*-isomers rapidly converted to the *Z*-isomers. The conversion of the **NRM** was essentially complete within 10 min. In the case of **CS**, a significant fraction of *E*-isomers remained present even after prolonged irradiation, which pointed to a photostationary state. Considering the differences in analysis techniques and experimental conditions the agreement between the results from NMR and HPLC is satisfactory.

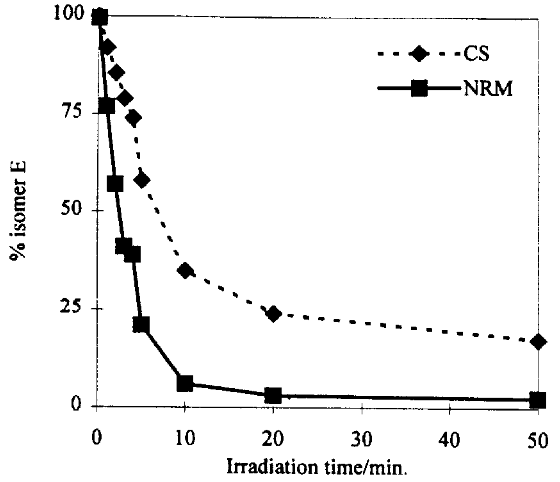


Figure 4. Extent of isomerization as a function of UV exposure as measured by HPLC.

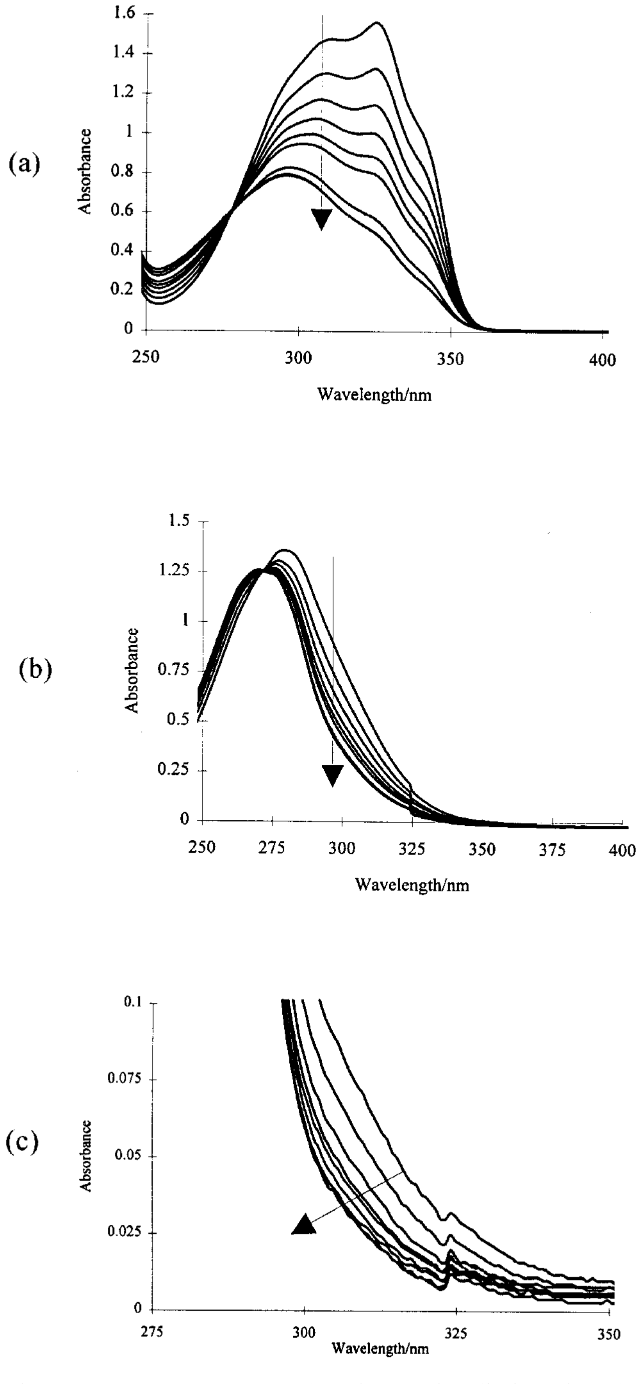


Figure 5. UV spectra as a function of irradiation time for (*A*) **CS**, (*B*) **NRM**, (*C*) copolymer. The lines represent (in the order indicated by the arrow): 0, 1, 2, 3, 4, 5, 10, 20, and 50 min of irradiation. Note that the lines for the longest irradiation times may overlap one another. The small peak in figure 5 (*b*) and (*c*) at approximately 323 nm is an artifact of the equipment.

3.5. *UV spectra*

UV spectra of solutions of the monomers and the compolymer in dichloromethane and acetonitrile were recorded. The concentrations used were the same as those used in the HPLC experiments (approx. 5×10^{-5} M). The trends in the spectra were the same for both solvents. Figure 5 shows only the results for dichloromethane. The absorption spectrum of **CS** reveals major changes during the irradiation process. The absorption at the absorption maximum decreased continuously. No further major changes occurred after 10 min or irradiation. An isosbestic point was observed at 277·5 nm; this provides further evidence for the absence of major side reactions. The differences in UV behaviour between **NRM** and **RM** were small. The results obtained for **NRM** are shown in figure 5 (*b*). The changes in the absorption spectrum are smaller than for **CS**; the maximum of the absorption peak shifts to lower wavelengths. An isosbestic point was observed at 271·5 nm, indicating that in this case too side reactions are limited. The changes in the UV spectra of the isomerizations in the copolymer are obscured by the absorptions of the **CN6** repeat units. The absorption tail at high wave lengths, however, shows the same trend as that observed for **NRM**. The results for **NRM** are in line with the results obtained by Yarmolenko *et al.* for a related compound [17].

3.6. *Influence of UV irradiation on the pitch*

The pitches of the compounds were measured for solutions in a commercial active matrix liquid crystal mixture (ZLI 4792) using a wedge cell. The results obtained for the helical twisting power are shown in figure 6. It is clear that the pitch of the mixture of the liquid crystal and **NRM** was dramatically influenced by the *E*–*Z*-isomerization process. Within a few minutes of irradiation the helical twisting power almost vanished. These results are in line with those obtained for related compounds reported by Yarmolenko *et al.* [17]. The helical twisting power of the *Z*-isomer is probably small. The differences between **NRM** and **RM** were small (only the results obtained for **NRM** are shown). The kinetics of the changes are in line with those derived from the HPLC data. Figure 6 compares the influence of the isomerization process on the helical twisting power of the copolymer of **RM** and **CN6** with that of **NRM**. The solubility of the copolymer in ZLI 4792 was too low. Therefore E7 was used to dissolve the copolymer (1·6 wt % solution). For the comparison, the pitch of the copolymer was recalculated to the fraction of chiral dopant (16 mol %). It is clear that the isomerizations of the two dopants proceeded in a practically identical manner despite the differences in the liquid crystal host and chemical constitution. Only at longer irradiation times do some deviations occur. The accuracy of the pitch measurements at long pitch values is low, because of the small number of Grandjean lines. Another reason may be that the last remnant of chiral units in the copolymer was sterically less accessible for the isomerization process.

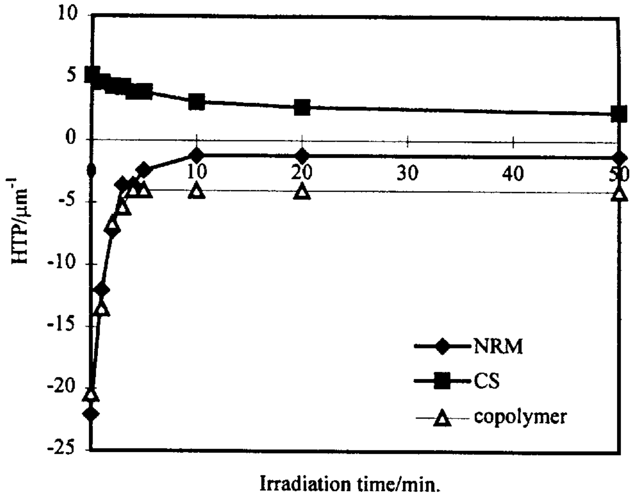


Figure 6. Helical twisting powers of the chiral dopants in ZLI 4792 (**NRM** and **CS**) or E7 (copolymer) as a function of UV exposure time. The helical twisting power presented for the copolymer is based on the fraction of chiral units. The value for the copolymer is *c*. 6 times lower.

The changes in the pitch induced by the isomerization of **CS** were in the order of a factor of 2. After 50 min, a fraction of 20–25% of *E*-compound can be expected to be present in solution as determined by HPLC. This result indicates that the difference in helical twisting power between the isomers of **CS** is much less than that between the isomers of **NRM**.

Figure 7 (*a*) shows the effects of the addition of small amounts of the commercial chiral dopant S811 to a solution of **CS** in ZLI 4792 on the absolute values of the reciprocal pitch. In a control experiment it was confirmed that the pitch of S811 in this liquid crystal mixture did not change upon exposure to UV light. From the intersection points with the *y*-axis it is clear that the helical twisting powers of S811 and **CS** are of opposite signs. The pitch increased with increasing concentrations of S811. During irradiation, the twisting power of **CS** decreased. Therefore, the pitch of the mixture of **CS**, S811, and the liquid crystal host increased upon UV exposure until the pitch of **CS** was the same as that of S811. In this case very few or no Grandjean lines were visible in the wedge cell and the pitch was infinite. Upon prolonged exposure, the difference in twisting power between the dopants increased again and the pitch of the mixture decreased. In this case the pitch must have been of opposite handedness (see next section). When the amount of S811 in the mixture was large, the twisting sense was already determined by the twisting sense of S811. UV exposure directly led to a decrease in the pitch. The same effects are observable in figure 7 (*b*) for **NRM** and the commercial chiral dopant of opposite handedness R811. In these experiments, much shorter irradiation times were taken to get a better indication of the position of the minima of the graphs.

3.7. *Experiments with TN cells*

The cells were filled with a mixture of **CS** S811 and ZLI 4792 (0·29 wt % S811, 1·1 wt % **CS**). The mixture was chosen such that the twisting sense was dominated by **CS**. The twisting sense of the mixture was identical to the twisting sense imposed by the alignment layers (right-handed). The twisting sense of the TN cell could be easily determined from the luminance values of the addressed TN cell at oblique polar viewing angles and various azimuthal viewing angles [24]. The twisting

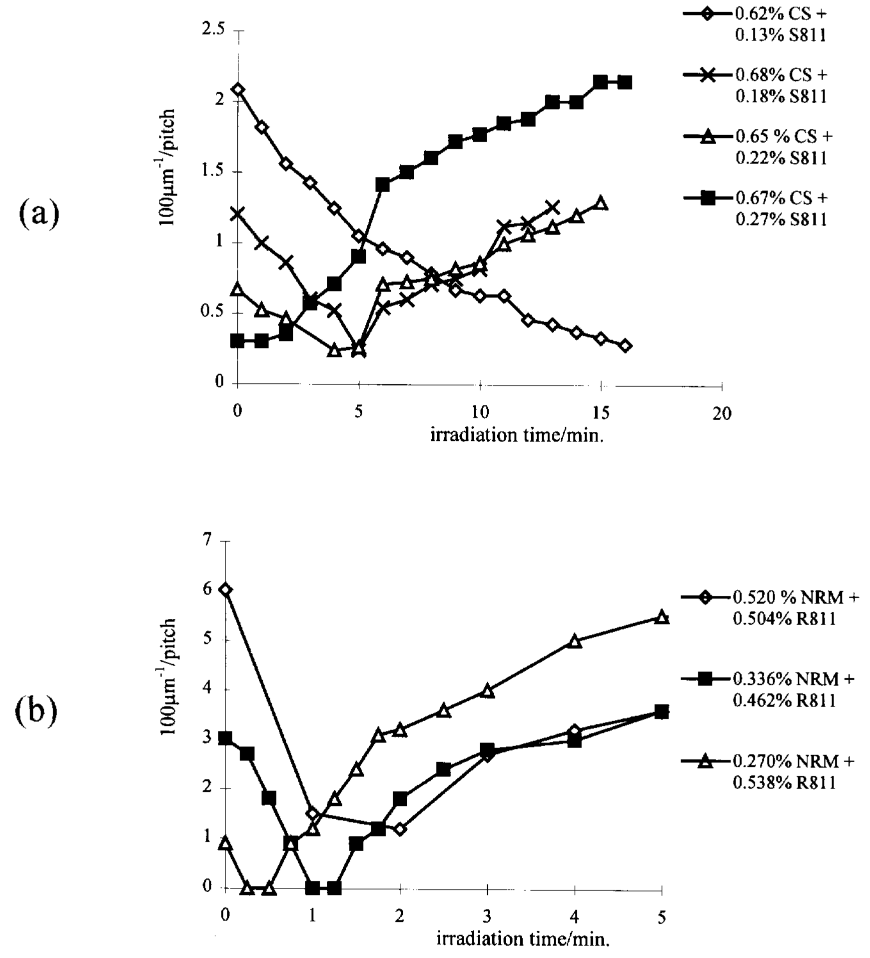


Figure 7. The reciprocal pitch as a function of irradiation time for mixtures of photoisomerizable dopants, S/R 811 and ZLI 4792.

sense of the TN cells before illumination was as expected. After illumination of the cell, the twisting sense was reversed. The time necessary for reversal of the twisting sense coincided with the peak maximum in figure 7 corresponding to the same S811/CS ratio (6 min). It was also possible to generate patterns in the liquid crystal with opposite twisting senses by illuminating the cell through a mask.

As the dopants are not fixed in place, the life time of the patterns is limited. Therefore the experiments were repeated with the copolymer. It was expected that the higher molecular weight of the copolymer would lengthen the time scales for diffusion. A 4·3 µm cell was filled with a mixture consisting of 2·4 wt % copolymer, 0·58 wt % R811 and 97 wt % E7. The rubbing directions were aligned according to a left-handed twist; initially, the twist of the cell was left-handed. The cell was irradiated through a mask. After illumination the irradiated parts showed a right-handed twist and the non-irradiated parts still showed the original left-handed twist. The cell was provided with polarizers (normally white) and addressed at a low voltage (3–4 V). At oblique viewing angles the differences in viewing angle characteristics could be easily observed (figure 8). As expected the viewing angle characteristics of the irradiated domains were rotated 90° with respect to the non-irradiated domains. The patterns remained intact for periods up to several weeks.

4. Conclusions

The photoisomerization reactions of the compounds investigated proceeded rapidly and without the generation of side products. All the investigated chiral dopants showed a strong dependence of the cholesteric pitch upon *E*–*Z*-isomerization. Substantial changes in pitch were induced by the isomerization of the menthone in particular. The inclusion of the menthone derivatives in a nematic side group liquid crystalline copolymer resulted in polymers with properties similar to those of the low molecular mass compounds.

Mixtures of the isomerizable dopants, and dopants with an opposite twisting sense, in standard commercial nematic liquid crystal hosts could be converted from a left-handed twisting sense to a right-handed twisting sense

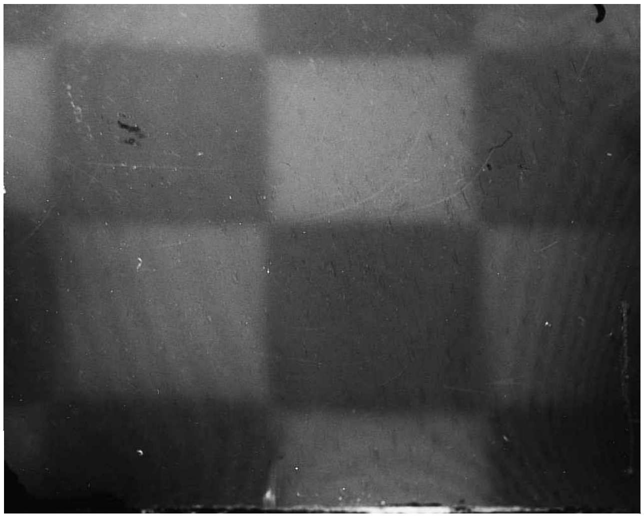


Figure 8. Photomicrograph of the dual-domain TN test cell for oblique viewing angles (approximately 35°).

or vice versa. This concept could be used to prepare dual-domain TN cells. The possibility of preparing dual-domain TC cells by using a fully external method implies a significant potential advantage over the laborious techniques presented in the literature. The viewing angle properties of the UV-irradiated parts of the TN cell were rotated 90° with respect to the non-irradiated parts. Because the viewing angle properties of the two types of domains will be mixed for all azimuthal viewing angles, the viewing angle dependence of the display will decrease. Owing to diffusion, the life times of the patterns were limited in the present version, even in the case of the copolymer. For improved versions, the copolymer will have to be crosslinked to some extent to form a permanent gel (see for example [25]).

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