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Synthesis and properties of chiral stilbene diacrylates

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Two chiral and isomerizable liquid crystalline diacrylates were synthesized. The purpose of these compounds was to tune the helical twisting power of cholesteric materials containing these compounds by means of an *E–Z* photoisomerization of the photoactive group derived from stilbene. The photochemical behaviour of these compounds was studied with the aid of two model compounds containing the same isomerizable mesogenic group. The mesogenic group derived from 4-(4-hydroxybenzoyloxy)-4′-hydroxystilbene decomposes upon irradiation. Its isomer, derived from 4-(4-hydroxyphenoxycarbonyl)-4′-hydroxystilbene, shows a clean *E–Z* isomerization. The HTP of the chiral diacrylate derived from the latter mesogenic group changes from 7 to 3 μm^{-1} in dilute nematic solution. Colour changes in a cholesteric material containing this compound were observed. The effect was very dependent on temperature and concentration due to the strong smectic character of this diacrylate.

1. Introduction

Cholesteric liquid crystalline materials have attracted much attention due to their capability to reflect circularly polarized light. The helical nature of this liquid crystalline phase means that light of perpendicular incidence is reflected as circularly polarized light, the wavelength of reflection (λ) being given by:

$$\lambda = n/(\mathrm{HTP}*x)$$

where HTP is the helical twisting power of the chiral component in the system, x is the weight fraction of this chiral component in a nematic solution, and n is the mean refractive index which is dependent on the structures of the liquid crystals and thus on the weight fraction x. The bandwidth ($\Delta\lambda$) of the reflection band is given by:

$$\Delta\lambda = \Delta n/(\mathrm{HTP}*x)$$

and depends on the birefringence (Δn) of the liquid crystalline system. Δn is also dependent on the weight fraction x.

On the basis of this property, several applications have been explored, ranging from paints to optical components [1, 2]. The reflection colour can be chosen on the basis of the ratio of nematic to chiral liquid crystals. The colour can be changed after applying such a mixture by making use of the thermochromic effect [3] and of the photochromic effect. In the first case the thermal dependence of the HTP plays a role and in the second case the HTP of the system is changed by a photochemical reaction. On the basis of the photochemical process, polymers whose reflection wavelengths can be changed from UV to infrared simply by changing the UV dose were prepared [4–6]. The chiral component of these polymers, which is derived from menthone, undergoes an *E* to *Z* isomerisation under UV irradiation. This is accompanied by a large drop in helical twisting power (HTP) and thus an increase in the reflection wavelength. Several applications of these polymers have been explored [6, 7], with the most promising example being cholesteric colour filters for use in LCDs [8].

A disadvantage of these polymers is their low thermal and mechanical stability, which means that they are not always suitable for optical applications. Very stable liquid crystalline optical components can be obtained with the aid of liquid crystalline diacrylates or mixtures of liquid crystalline monoacrylates and diacrylates that are polymerized to form very stable crosslinked films. Crosslinking is normally carried out by photopolymerization, using photoinitiators, in order to make this process temperature-independent [9]. This is important because the physical properties of the monomers are often temperature-dependent as a result of the liquid crystalline phase behaviour of these compounds [10]. In the case of cholesteric materials, mixtures of chiral compound **1** and nematic compound **3** form very stable monochromic reflecting layers after polymerization [11]; see table 1 and 2 for structures. Using special polymerization techniques, mixtures of **1** and nematic monoacrylates were used to form organic mirrors that can be applied as broadband polarizers for LCDs [1, 2].

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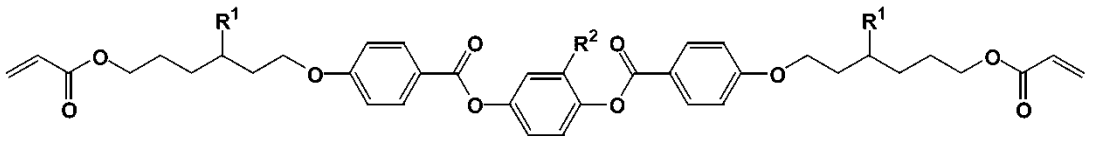
Table 1. Liquid crystalline transition temperatures of cholesteric compounds **1** and **2** and of nematic compound **3**.



Compound	R^1	R^2	Phase transitions/°C
1	CH_3	H	Cr–67–N*–79–I
2	CH_3	CH_3	Cr–45–N*–54–I
3	H	CH_3	Cr–86–N–116–I

The HTP of compounds **1** and **2** is approximately $7\,\mu m^{-1}$. In order to change this value photochemically, it was decided to change one of the aromatic ester groups of **1** into a double bond to form compound **4**. This stilbene derivative is expected to undergo *E–Z* isomerization upon irradiation, and the HTP of the *Z* isomer is expected to differ from that of the *E* isomer. If a grey scale mask is used, it is possible to vary the irradiation dose in order to obtain coloured patterns in a film of these materials, in the same way as described for photochromic polymers [5]. The acrylate groups of **4** can be used to form stable crosslinked polymer films by thermal polymerization or other polymerization techniques after the colour pattern is formed [8, 12].

This paper deals with the synthesis and properties of stilbene derivative **4** and of its isomer **5**.

2. Experimental

2.1. *Materials and methods*

The liquid crystal E7 (a mixture of nematic liquid crystals derived from cyanobiphenyl) was obtained from Merck. Compounds **1**, **2** and **3** were made according to literature procedures [11, 13, 14]. Literature procedures were also used to prepare **7** [11, 13], **9** [15], **13** [11, 13] and **32** [16]. All other chemicals were obtained from Aldrich or Acros. Synthetic methods are outlined in schemes 1–3.

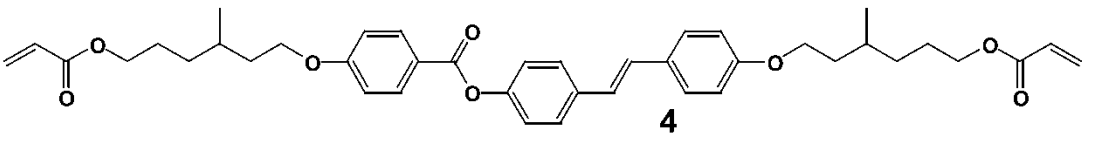
UV spectra were recorded with the aid of a Unicam UV2-100 spectrometer in an acetonitrile solution or pure in a 5 μm cell coated with rubbed polyimide (Linkam). NMR spectra were recorded with the aid of a Bruker DP300 spectrometer in a deuteriated chloroform or dichloromethane solution. The ^1H and ^{13}C NMR data were fully consistent with the required structures and confirmed the purity of the final products. The NMR data of compounds **4** and **5** are given. Irradiation of the samples was performed with a Philips pl-10 (365 nm) lamp. The intensity at the sample surfaces was $0.25\,mW\,cm^{-2}$.

Phase transition temperatures were measured with a Perkin Elmer DSC-7 and with a polarizing microscope fitted with a Mettler FP52 hotstage. The helical twisting power was determined using the Grandjean–Cano method [17]. Wedge cells (EHC Japan, $\tan\alpha = 0.0083$) were filled with solutions of compounds **1**, **2**, **4** or **5** in E7. The total amount of chiral compounds did not at any time exceed 2 wt%. The distance between the disclination lines was measured before and after irradiation with 365 nm light.

2.2. *Synthesis of (E)-(S,S)-4-[4-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy]-4′-(6-acryloyloxy-3-methylhexyloxy)stilbene (**4**)*

2.2.1. *(S)-6-(4-Hydroxymethylphenyloxy)-4-methylhexanol (**8**)*

A mixture of 12.4 g of 4-hydroxymethylphenol (**6**), 19.5 g of (*S*)-3-methyl-6-hydroxybromohexane (**7**), 20.7 g of potassium carbonate and 100 ml of butanone was heated under reflux for 20 h. After evaporation of the butanone, 150 ml of diethyl ether was added. The ethereal layer was then extracted with 50 ml of a 10%



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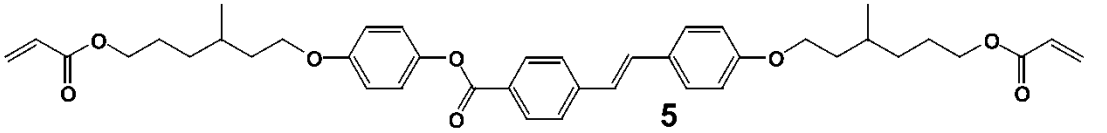

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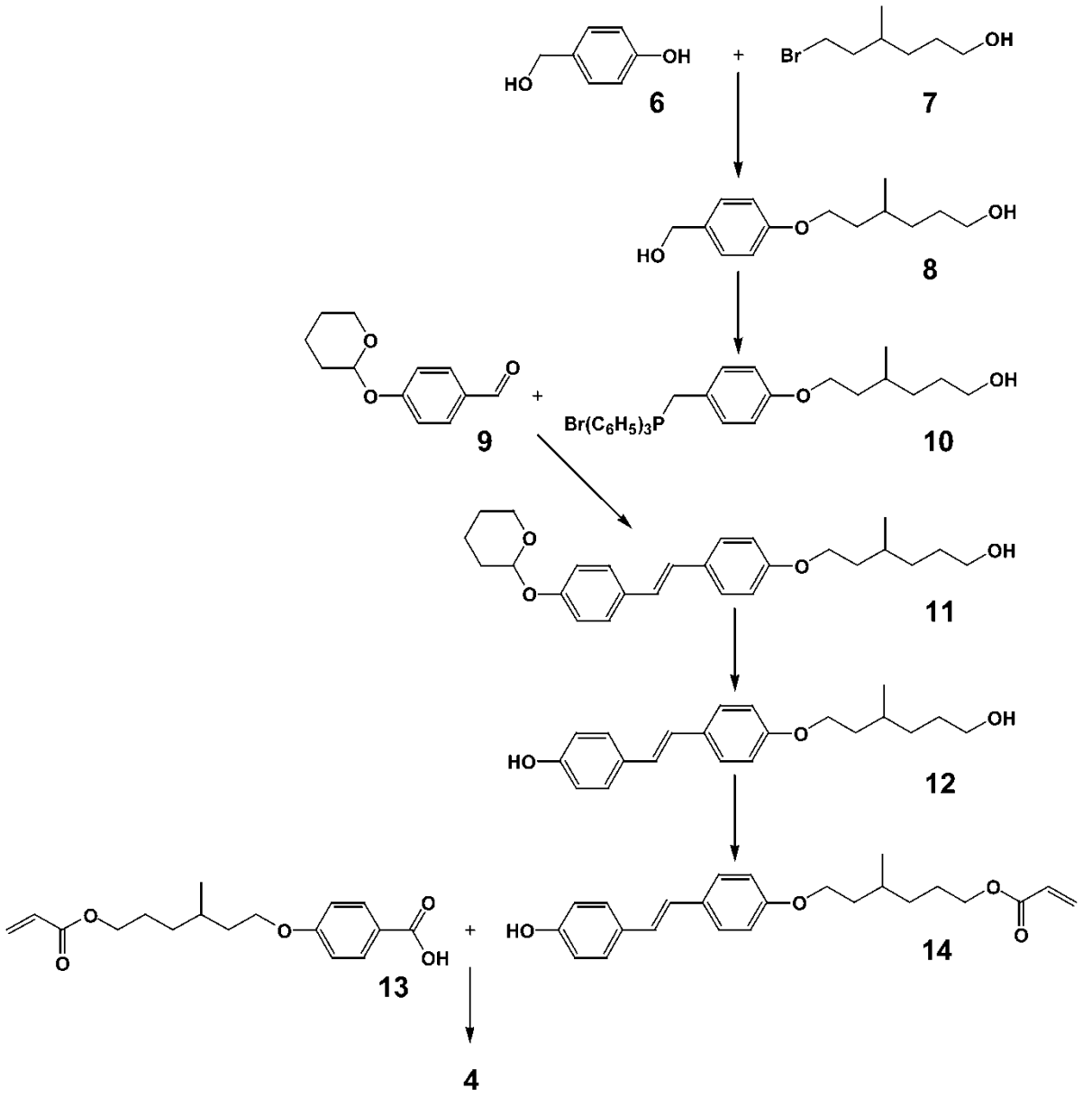


Scheme 1. Synthesis of (*E*)-(*S*,*S*)-4-[4-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy]-4′-(6-acryloyloxy-3-methylhexyloxy)stilbene (**4**).

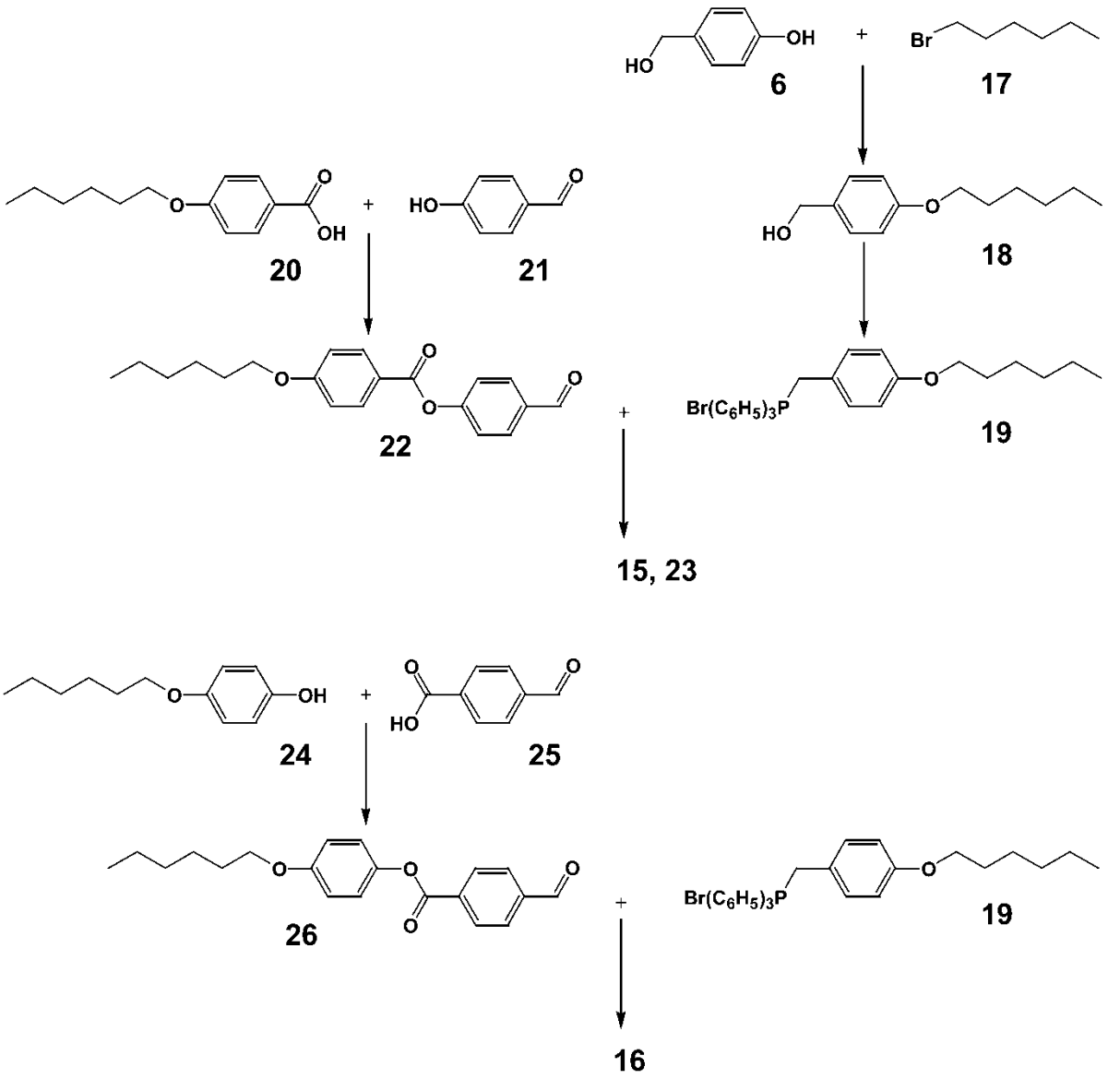
aqueous sodium hydroxide and 50 ml of brine. The crude product obtained after drying over magnesium sulfate and evaporation of the diethyl ether was distilled in a Kugelrohr apparatus at 100°C and 0.3 mb; 14.3 g (60%) of the product was obtained as a clear oil which solidified on standing.

2.2.2. *(S)-4-(6-Hydroxy-3-methylhexyloxy)phenylmethyltriphenylphosphonium bromide (**10**)*

A mixture of 11.9 g of compound **8**, 17.2 g of triphenylphosphonium bromide and 100 ml of dichloromethane was stirred for 16 h. A clear solution was obtained. After evaporation of the dichloromethane 28.2 g (100%) of a viscous liquid was obtained which vitrified at room temperature. NMR analysis revealed that it was pure enough to perform the next step.

2.2.3. *(E)-(S)-4-(6-Hydroxy-3-methylhexyloxy)-4′-(tetrahydropyran-2-yloxy)stilbene (**11**)*

A solution of lithium ethoxide was prepared from 200 ml of ethanol and 350 mg of lithium. To this solution were added 10.3 g of 4-(tetrahydropyran-2-yloxy)benzaldehyde (**9**) and 28.2 g of compound **10**. After stirring for 16 h, 20 ml of water was added and the solution was held at −18°C. The precipitate was collected by filtration,



Scheme 2. Synthesis of (*E*)-4-(4-hexyloxybenzoyloxy)-4′-hexyloxystilbene (**15**), (*Z*)-4-(4-hexyloxybenzoyloxy)-4′-hexyloxystilbene (**23**) and (*E*)-4-(4-hexyloxyphenoxycarbonyl)-4′-hexyloxystilbene (**16**).

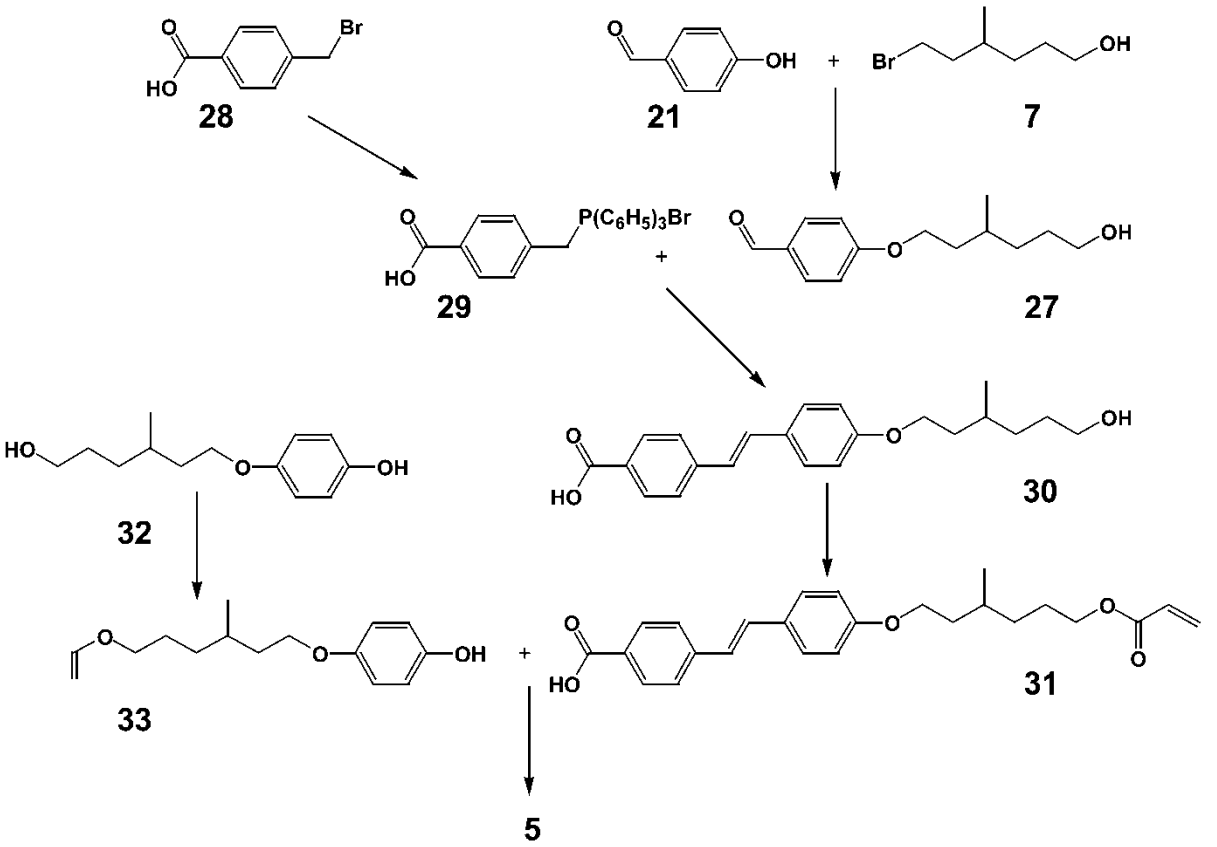
washed with 100 ml of an ethanol/water (1/1) mixture and dried over silica in a desiccator; 6.8 g (33%) of the product was obtained as a white solid.

2.2.4. *(E)-(S)-4-(6-Hydroxy-3-methylhexyloxy)-4′-hydroxystilbene (**12**)*

A solution of 6.8 g of compound **11** and 0.5 ml of concentrated hydrochloric acid in 30 ml of ethanol was stirred at 50°C for 3 h. The solution was added dropwise to 150 ml of water, whereupon the product precipitated; 4.3 g (80%) was obtained after washing with water and drying over silica in a desiccator.

2.2.5. *(E)-(S)-4-(6-acryloyloxy-3-methylhexyloxy)-4′-hydroxystilbene (**14**)*

Acryloyl chloride (1.3 g) was added to a solution of 4.3 g of compound **12** and 1.8 g of *N*,*N*-dimethylaniline in 30 ml of dichloromethane, cooled in an ice-bath. After stirring for 20 h at room temperature, the dichloromethane solution was extracted twice with 25 ml of 2M hydrochloric acid and 20 ml of water; 4.8 g (95%)



Scheme 3. Synthesis of (*E*)-4-[4-(6-acryloyloxy-(*S*)-3-methylhexyloxy)phenyloxycarbonyl]-4′-(6-acryloyloxy-(*S*)-3-methylhexyloxy) stilbene (**5**).

of a white solid was obtained after drying over magnesium sulphate and evaporation of the dichloromethane.

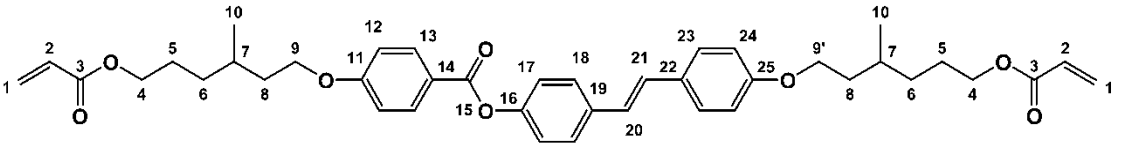
2.2.6. *Synthesis of (E)-(S,S)-4-[4-(6-acryloyloxy-3-methylhexyloxy)benzoyloxy]-4′-(6-acryloyloxy-3-methylhexyloxy)stilbene (**4**)*

N,*N*′-dicyclohexyl carbodiimide (2.6 g) was added to a mixture of 4.8 g of compound **14**, 2.6 g of (*S*)-4-(6-acryloyloxy-3-methylhexyloxy)benzoic acid (**13**), 160 mg of 4-*N*,*N*-dimethylaminopyridine and 30 ml of dichloromethane, stirred in an ice-bath. After stirring for 20 h at room temperature, the mixture was filtered and the dichloromethane evaporated; 5.8 g (70%) of the product was obtained as a white solid after elution over silica with dichloromethane/ethyl acetate 97/3 and crystallization from 2-propanol. ^{1}H NMR: 8.13 (d, 2H, $J=8.6$, H^{13}), 7.52 (d, 2H, $J=8.6$, H^{18}), 7.43 (d, 2H, $J=8.6$, H^{23}), 7.17 (d, 2H, $J=8.6$, H^{17}), 7.03 (d, 2H, $J=16.6$, H^{20}), 6.92 (d, 2H, $J=16.6$, H^{21}), 6.90 (d, 2H, $J=8.6$, H^{12}), 6.87 (d, 2H, $J=8.6$, H^{24}), 6.42 (dd, 2H, $J_1=17.3$, $J_2=1.5$, H^{1-cis}), 6.13 (dd, 2H, $J_1=17.3$, $J_2=10.5$, H^2), 5.82 (dd, 2H, $J_1=10.5$, $J_2=1.5$, $H^{1-trans}$), 4.15 (t, 4H, $J=7.0$, H^4), 4.0+4.06 (m, 4H, $H^9+H^{9'}$), 1.95−1.20 (m, 14H, $H^5+H^6+H^7+H^8$), 0.97 (d, 6H, J=7.0, H^{10}). ^{13}C NMR: 166.6 (C^3), 165.3 (C^{15}), 163.7 (C^{11}), 159.2 (C^{25}), 150.5 (C^{16}), 135.7 (C^{19}), 132.7 (C^{13}), 130.9 (C^1+C^{22}), 128.9 (C^2), 128.7 (C^{20}), 128.1 (C^{23}), 127.3 (C^{18}), 126.0 (C^{21}), 123.3 (C^{17}), 122.0 (C^{14}), 115.1 (C^{12}), 114.6 (C^{24}), 66.7 ($C^{9'}$), 66.5 (C^9), 65.2 (C^4), 36.4 (C^8), 33.5 (C^6), 29.9 (C^7), 26.4 (C^5), 19.8 (C^{10}). Elemental analysis: calc. C 73.63, H 7.23; found C 73.8, H 7.3 %.

2.3. *Synthesis of (E)-4-[4-(6-acryloyloxy-(S)-3-methylhexyloxy)phenyloxycarbonyl]-4′-(6-acryloyloxy-(S)-3-methylhexyloxy)stilbene (**5**)*

2.3.1. *(S)-4(-6-Hydroxy-3-methylhexyloxy)benzaldehyde (**27**)*

A solution of 4 g of sodium hydroxide, 12.2 g of 4-hydroxybenzaldehyde (**21**) and 19.5 g of (*S*)-3-methyl-6-hydroxybromohexane (**7**) in 150 ml of ethanol was heated at reflux for 20 h. After evaporation of the ethanol, the product was dissolved in 200 ml of diethyl ether which was then extracted twice with 50 ml of 10% aqueous sodium hydroxide and 50 ml of brine; 20.1 g



(85%) of the product was obtained after drying over magnesium sulphate and evaporation of the diethyl ether.

2.3.2. *(4-Carboxybenzyl)triphenylphosphonium bromide (**29**)*

A solution of 10.7 g of 4-bromomethylbenzoic acid (**28**) and 13.1 g of triphenylphosphine in 150 ml of toluene was heated at 115°C for 5 h under a nitrogen atmosphere. The solid obtained was collected by filtration; 22.6 g (94%) of the product was obtained after washing with toluene and drying at 60°C in a vacuum.

2.3.3. *(E)-4-Carboxy-4′-(6-hydroxy-(S)-3-methylhexyloxy)stilbene (**30**)*

A solution of lithium ethoxide was prepared from 200 ml of ethanol and 410 mg of lithium. To this solution were added 7.1 g of (*S*)-4-(-6-hydroxy-3-methylhexyloxy)benzaldehyde (**27**) and 14.3 g of compound **29**. After stirring for 2 h at room temperature, the precipitated intermediate lithium salt was obtained by filtration. It was washed with 50 ml of ethanol and mixed with 60 ml of ethanol and 1.5 ml of conc. hydrochloric acid. This mixture was heated until solution was complete; it was then cooled, whereupon the product precipitated. 2.6 g (25%) of the product was obtained after washing with ethanol and drying over silica in a desiccator.

2.3.4. *(E)-4-Carboxy-4′-(6-acryloyloxy-(S)-3-methylhexyloxy)stilbene (**31**)*

A mixture of 2.6 g of compound **30**, 1.0 g of *N*,*N*′-dimethylaniline, 0.72 g of acryloyl chloride, 4.2 mg of 2,6-di-*tert*-butyl-4-methylphenol and 13 ml of 1,4-dioxane was heated at 60°C for 2 h. After cooling, a mixture of 35 ml of water and 2 ml of conc. hydrochloric acid was added dropwise in order to precipitate the product; 2.4 g (82%) of the product was obtained as a solid after washing with ethanol and drying over silica in a desiccator.

2.3.5. *4-(6-Acryloyloxy-(S)-3-methyl-hexyloxy)phenol (**33**)*

This compound was made in the same way as described above for compound **14**, starting from 4-(6-hydroxy-(S)-3-methylhexyloxy)phenol (**32**). The product was obtained as an oil in 85% yield.

2.3.6. *Synthesis of (E)-4-[4-(6-acryloyloxy-(S)-3-methylhexyloxy)phenyloxycarbonyl]-4′-(6-acryloyloxy-(S)-3-methylhexyloxy)stilbene (**5**)*

This compound was made in the same way as described for compound **4**, starting from compounds **31** and **33**. The product was obtained as a white powder in 55% yield. ^{1}H NMR: 8.16 (d, 2H, $J=8.6$, H^{17}), 7.61 (d, 2H, $J=8.6$, H^{18}), 7.48 (d, 2H, $J=8.6$, H^{23}), 7.22 (d, 2H, $J=16.6$, H^{20}), 7.11 (d, 2H, $J=8.6$, H^{13}), 7.03 (d, 2H, $J=16.6$, H^{21}), 6.93 (d, 2H, $J=8.6$, H^{12}), 6.90 (d, 2H, $J=8.6$, H^{24}), 6.42 (dd, 2H, $J_1=17.3$, $J_2=1.5$, H^{1-cis}), 6.13 (dd, 2H, $J_1=17.3$, $J_2=10.5$, H^2), 5.82 (dd, 2H, $J_1=10.5$, $J_2=1.5$, $H^{1-trans}$), 4.18 (t, 4H, $J=7.0$, H^4), 4.0+4.02 (m, 4H, $H^9+H^{9'}$), 1.95−1.25 (m, 14H, $H^5+H^6+H^7+H^8$), 0.97 (d, 6H, J=7.0, H^{10}).
^{13}C NMR: 166.3 (C^3), 165.3 (C^{15}), 159.3 (C^{25}), 156.7 (C^{11}), 144.3 (C^{14}), 142.8 (C^{19}), 131.6 (C^{20}), 130.9 (C^1+C^{17}), 129.3 (C^{16}), 128.9 (C^2), 128.5 (C^{23}), 127.8 (C^{22}), 126.5 (C^{18}), 125.6 (C^{21}), 122.8 (C^{13}), 115.4 (C^{12}), 115.2 (C^{24}), 66.8 ($C^{9'}$), 66.5 (C^9), 65.2 (C^4), 36.4 (C^8), 33.5 (C^6), 29.9 (C^7), 26.4 (C^5), 19.8 (C^{10}). Elemental analysis: calc. C 73.63, H 7.23; found C 74.0, H 7.3 %.

2.4 *Synthesis of (E)-4-(4-hexyloxybenzoyloxy)-4′-hexyloxystilbene (**15**) and (Z)-4-(4-hexyloxybenzoyloxy)-4′-hexyloxystilbene (**23**)*

2.4.1. *4-Hexyloxyphenylmethanol (**18**)*

This compound was made in the same way as described for compound **8**, starting from 4-hydroxymethylphenol (**6**) and bromohexane (**17**). The product was obtained as a solid in 60% yield.

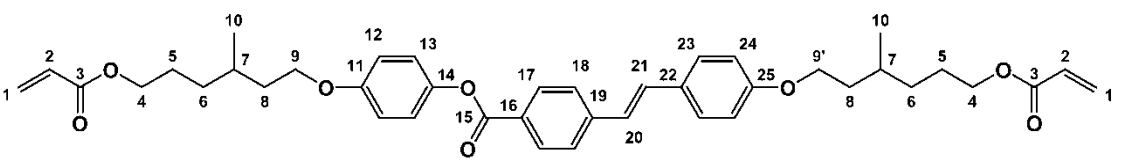
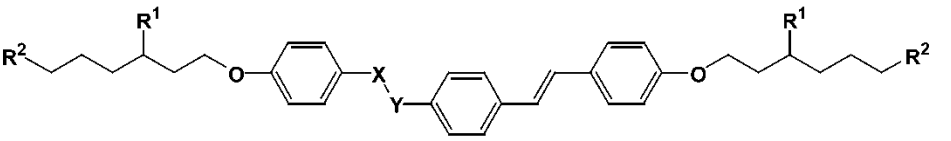


Table 2. Liquid crystalline transition temperatures of chiral diacrylates **4** and **5** and of model compounds **15** and **16**.



	X-Y	R^1	R^2	Phase transitions/°C
4	CO-O	CH_3	acrylate	Cr–67–SmA–90–CH–135–I
5	O-CO	CH_3	acrylate	Cr–67–SmA–112–I
15	CO-O	H	H	Cr–134–SmA–167–N–253–I
16	O-CO	H	H	Cr–132–SmX–141–SmA–243–I

2.4.2. *(4-Hexyloxybenzyl)triphenylphosphonium bromide (**19**)*

This compound was made in the same way as described for compound **10**, starting from 4-hexyloxyphenylmethanol (**18**). The product was obtained as a white powder in 94% yield.

2.4.3. *4-Formylphenyl 4-hexyloxybenzoate (**22**)*

2.9 g of *N*,*N*′-dicyclohexyl carbodiimide was added to a mixture of 3.1 g of 4-hexyloxybenzoic acid (**20**), 1.7 g of 4-hydroxybenzaldehyde (**21**), 170 mg of 4-*N*,*N*-dimethylaminopyridine and 35 ml of dichloromethane cooled in an ice-bath. The mixture was stirred for 5 h at room temperature and filtered through a thin layer of silica; 3.4 g (75%) of the product was obtained as white crystals after evaporation of the dichloromethane and crystallization from ethanol.

2.4.4. *Synthesis of (E)-4-(4-hexyloxybenzoyloxy)-4′-hexyloxystilbene (**15**) and (Z)-4-(4-hexyloxybenzoyloxy)-4′-hexyloxystilbene (**23**)*

5.5 ml of 50% aqueous sodium hydroxide was added dropwise to a vigorously stirred solution of 5.6 g of compound **19** and 3.4 g of compound **22** in 25 ml of dichloromethane. After the solution had been stirred for an hour, 20 ml of dichloromethane and 20 ml of water were added. After separation, the dichloromethane was evaporated and the solid obtained was washed with 25 ml of ethanol. The ethanolic solution was kept to obtain compound **23**; 1.4 g (26%) of product **15** was obtained as white crystals after washing the solid twice with 25 ml of ethanol followed by crystallization from ethyl acetate.

The ethanolic solution from the first washing was evaporated and the solid obtained was crystallized three times from 3 ml of ethanol to obtain 1.1 g (21%) of product **23** as a white powder with m.p. = 53°C.

2.5. *Synthesis of (E)-4-(4-hexyloxyphenoxycarbonyl)-4′-hexyloxystilbene (**16**)*

2.5.1. *4-Hexyloxyphenyl 4-formylbenzoate (**26**)*

This compound was made in the same way as described for compound **22**, starting from 4-hexyloxyphenol (**24**) and 4-formylbenzoic acid (**25**). The product was obtained as a white powder in 58% yield.

2.5.2. *(E)-4-(4-Hexyloxyphenoxycarbonyl)-4′-hexyloxystilbene (**16**)*

This compound was made in the same way as described for compound **15**, starting from compounds **19** and **26**. The product was obtained as white crystals in 27% yield.

3. Results and discussion

3.1. *Synthesis, properties and photochemistry of compound **4***

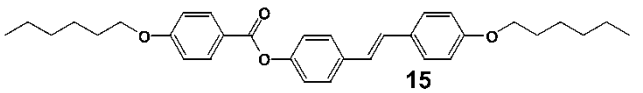
Scheme 1 shows the synthetic route used to prepare compound **4**. The chiral spacers between the aromatic system and the acrylate groups in **4** were formed from (*S*)-4-methyl-6-bromohexanol (**7**). This chiral compound was formed from (*S*)-citronellol or (*S*)-citronellyl bromide as described previously [11, 13]. Diol **8**, obtained after etherification of **6** and **7**, was converted into the Wittig reagent **10** by reaction with triphenylphosphonium bromide. This reaction is very selective. When molar equivalents were used at room temperature no reaction with the less reactive non-benzylic hydroxyl group was observed. The Wittig reaction between **10** and protected hydroxybenzaldehyde **9** was performed in ethanol in which the *trans*-compound **11** precipitated. The formation of protected aldehyde **9** has been described earlier [15]. Compound **12**, obtained after deprotection of **11**, was esterified with acryloyl chloride. *N*,*N*-Dimethylaniline was used as the base in this reaction. This medium is very selective; only the alcoholic hydroxyl group was acrylated. Even in the presence of an excess of acryloyl chloride, the phenolic

group was not esterified. Acrylic compound **14** thus obtained was esterified with acid **13** to form the final product **4**. The formation of acid **13,** starting with bromide **7**, has been described before in the synthesis of compounds **1** and **2** [11, 13].

The thermal data of compound **4** are presented in table 2. A comparison of these data with those of compound **1** (see table 1) reveals that compound **4** has a higher transition temperature from the cholesteric to the isotropic phase. This is most likely to be due to the stiffer mesogenic group of compound **4** which contains the stilbene moiety as compared with the more flexible ester functionality in the mesogenic group of compound **1**. This structural difference is probably also responsible for the appearance of a smectic phase, which is absent in compound **1**.

The HTP of compounds **1**, **2** and **4** were measured using the Cano wedge technique. The commercial mixture E7 was used as the host and the concentration of the compounds was below 2 wt %. Thus the chiral nematic phase behaviour was determined mainly by E7. In all cases a HTP of approximately $7\,\mu m^{-1}$ was measured. Thus the chiral interaction of these compounds with E7 is the same.

Upon irradiation of the sample containing **4** with UV light (365 nm), a decrease in the HTP was observed. Unfortunately, during this process the sample started to absorb and turned yellow–brown. This behaviour makes this compound unsuitable for use in optical components, because it should not absorb any visible light. In order to investigate the photochemical behaviour of this type of compound, it was decided to prepare the more simple stilbene derivative **15**, which contains the same photoactive group but does not contain the chiral groups and the acrylate groups. Both these groups are believed not to influence the photochemical behaviour of the central mesogenic group. For the purpose of comparison, isomer **16** was also prepared; in this compound the ester group is inverted as compared with **15**.



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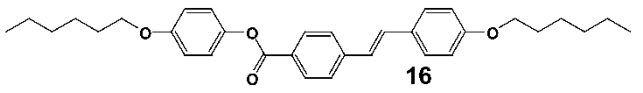
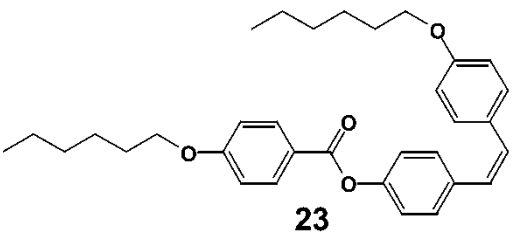


16

3.2. *Synthesis, properties and photochemistry of compounds 15 and 16*

The synthesis of **15** is very simple compared with that of **4** due to the absence of the chiral centre and the acrylate groups; scheme 2 shows the reaction steps. Wittig reagent **19** is made, starting from **6** and **17**, in the same way as reagent **10** was made, starting from **6** and **7** (see scheme 1). Because **22** contains an ester linkage, the Wittig reaction in ethanol with lithium ethanolate gave a poor yield due to alcoholysis of this ester bond. When this reaction was performed in a two-phase system containing dichloromethane and concentrated sodium hydroxide, this problem was avoided. In this reaction sequence, the use of the protected aldehyde **9** was avoided. In order to reduce the number of steps in scheme 1 used to prepare **4**; the reactions of scheme 2 were also tried with acid **20** replaced by **13** and Wittig reagent **19** by **10**. A very low yield of impure material was obtained. It is probable that the more polar acrylate group originating from **13** and the hydroxy group of **10** make the compounds more accessible for hydrolysis by the sodium hydroxide in this case.

A solution of **15** in acetonitrile was irradiated with 365 nm light and UV-Vis spectra were taken after various irradiation times. The spectra obtained before and after irradiation for 128 min are presented in figure 1. The appearance of absorption in the visible region is clearly observed. In order to record the spectrum of the *Z* isomer of **15**, which is expected to form upon irradiation, this isomer **23** was also isolated from the reaction mixture that was obtained during the formation of **15**.



23

The UV-Vis spectrum of **23** is also presented in figure 1. It showed no absorption in the visible region. From this figure it can be concluded that even if **23** were formed upon irradiation of **15**, it was not the only product. No trace of **23** could be observed upon HPLC analysis of a solution of **15** in acetonitrile after irradiation. A large number of peaks were observed in the HPLC trace even after a very short irradiation time. A solution of **15** in deuteriated dichloromethane was irradiated and ^{1}H NMR spectra were recorded. A multiplicity of peaks was observed, especially in the aromatic region, but the characteristic signals of the double bond of **23** around 6.5 ppm were not observed. Thus, compound **15** does not isomerize to its *Z* isomer **23** by irradiation with 365 nm light. If a solution of **23** in deuteriated dichloromethane was irradiated,

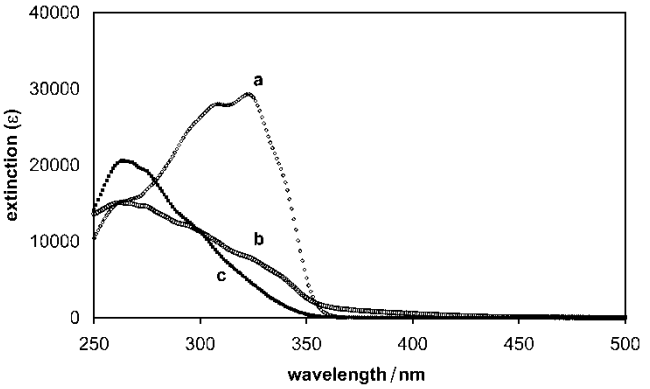


Figure 1. UV-Vis spectra of a solution of **15** in acetonitrile (*a*) before irradiation; (*b*) after 128 min of irradiation at 365 nm; (*c*) a solution of **23** in acetonitrile.

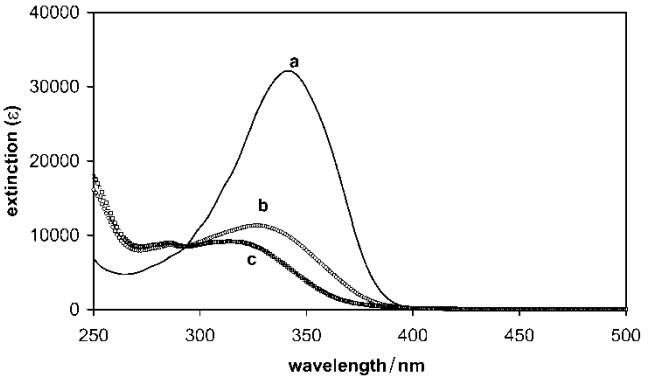


Figure 2. UV-Vis spectra of a solution of **16** in acetonitrile (*a*) before irradiation; (*b*) after 128 min of irradiation at 365 nm; (*c*) its *Z* isomer obtained by calculation.

yellowing also occurred, but at low conversion the signals of its *E* isomer **15** were clearly observed by ^{1}H NMR. After longer irradiation times the multiplicity of peaks was also observed, as in the irradiation of **15**. This is probably due to the photodegradation of **15**. From these results it can be concluded that the excited state of **15** will not form **23** but does form degradation products. The excited state of **23** is capable of the formation of **15**. Thus *E–Z* isomerization is not possible but *Z–E* isomerization is possible.

The degradation products formed upon irradiation of chiral compound **4** probably have a lower HTP than **4**. For that reason a drop in HTP value was observed during the irradiation in the Cano Wedge discussed in the preceding section.

Yellowing of liquid crystals derived from phenyl esters is a known phenomenon when high intensity UV light is used [18]. Normally a scission in the carboxy group known as a Norrish type I photochemical process occurs. The benzoyloxy and phenoxy types of radical formed may couple to form a derivative of benzophenone or other structures. This process, known as the Photo-Fries rearrangement, does indeed form compounds that absorb in the visible region. Although we were unable to detect such a compound from the photolysis mixture of **15**, it is possible that the ester scission occurs more easily than *E–Z* isomerization and that the fate of the radicals is more complicated than with simple phenyl esters. The main conclusion is that materials with this structure are useless for our purpose.

To determine whether molecules with a similar structure but having an inverted ester group can be isomerized, model compound **16** was prepared. Its synthesis is also outlined in scheme 2 and is very similar to that of the synthesis of **15**; specifically, aldehyde **22** was replaced by **26**. A solution of **16** in acetonitrile was irradiated with 365 nm light and UV-Vis spectra were taken after various irradiation times. The spectra before irradiation and after 128 min, after which no further changes were observed, are presented in figure 2. No absorption in the visible region was observed after irradiation. The *Z* isomer of **16** was not isolated but its UV spectrum could be calculated from the spectrum in the photostationary state (83% conversion, see later) using the spectrum before irradiation. This spectrum is also presented in figure 2. A solution of **16** in deuteriated dichloromethane was irradiated and ^{1}H NMR spectra were recorded. The characteristic signals of the double bond of the *Z* isomer around 6.5 ppm were observed. Upon prolonged irradiation a photostationary state was observed with a conversion of 83% of **16** to its *Z* isomer. After even longer irradiation small signals could be observed which might be attributed to degradation products. Thus, compound **16** does isomerize to its *Z* isomer by irradiation with 365 nm light. In this case the *E–Z* isomerisation is favoured over other photochemical reactions. Thus materials with this structure are suitable for our purpose and based on this, the synthesis of chiral compound **5** was undertaken.

3.3. *Synthesis, properties and photochemistry of compound* **5**

Scheme 3 shows the synthetic steps used to prepare compound **5**. Acid **30** was obtained from Wittig reagent **29** using two equivalents of lithium ethanolate followed by acidification. It was unnecessary to protect **29** by esterification. Acid **31** was obtained with the aid of acryloyl chloride and *N*,*N*-dimethylaniline. Although the mixed anhydride was believed to be a product, this anhydride probably reacts rapidly with the hydroxyl groups to form the product. Any mixed anhydride remaining due to an excess of acryloyl chloride, was probably hydrolysed upon the aqueous work-up. The synthesis of **32** from hydroquinone and bromide **7** has

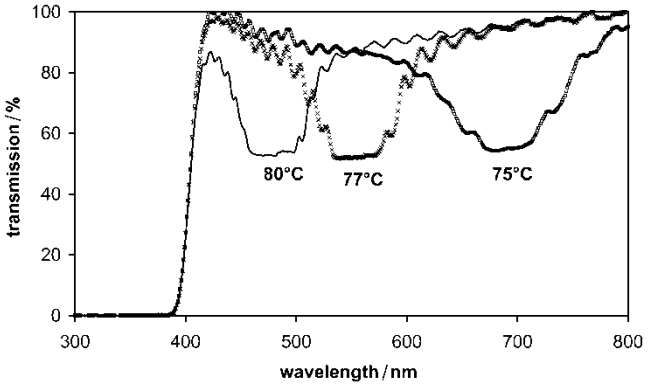


Figure 3. Transmission spectra of a 5 μm cell filled with a 1:1 mixture of **3** and **5** before irradiation.

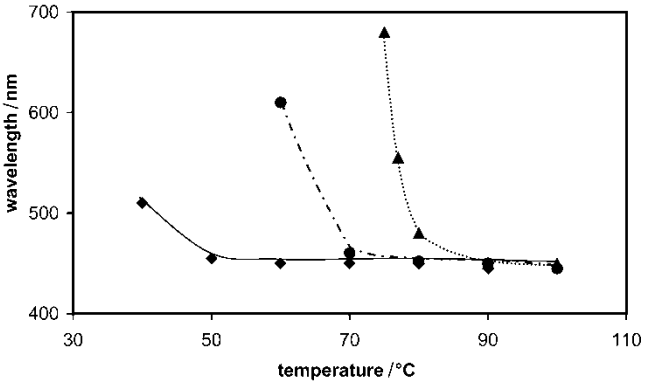


Figure 4. Transmission spectra of a 5 μm cell filled with a 1:1 mixture of **3** and **5** before irradiation (▲), and after irradiation for 30 (●) and 90 (■) min at 365 nm.

been described earlier [16]. Introduction of the acrylate group to form **33** was performed in the same way as described for **14** (scheme 1). Also the phenolic group in compound **32** was not reactive with acryloyl chloride if *N*,*N*-dimethylaniline was used as the base.

The thermal data for compound **5** are given in table 2. Comparison of these data with those of compound **4** (see table 1) reveal that compound **4** has a higher transition temperature to the isotropic phase, and the cholesteric phase is absent in **5**. This effect is not uncommon in these types of liquid crystals. Also in the case of non-chiral liquid crystalline diacrylates, strong effects on the phase behaviour upon inverting ester groups have been reported [19]. A similar trend was found by comparison of the thermal data of model compounds **15** and **16**, also shown in table 2.

The HTP of this compound was measured in the same way as for compounds **1**, **2** and **4** in E7. In all cases a HTP of approximately 7 μm^{-1} was measured. This shows similarity in the interaction of this class of compounds with E7. Upon irradiation the HTP of the solution with **5** dropped to 3 μm^{-1}. This change in HTP is in principle sufficient to change the colour of a cholesteric material from blue (400 nm) to infrared (800 nm). The spectra and spectral changes upon irradiation of **5** were equal to those measured with model compound **16**. Thus, the chiral moiety and the acrylate groups do not affect the photochemical behaviour of the central mesogenic group in **5**.

3.4. *Optical measurements*

In order to prepare a mixture which reflects visible light, compound **5** was mixed with the non chiral nematic compound **3** (see table 1). Figure 3 shows the transmission spectra of a 1:1 mixture in a 5 μm cell at different temperatures. The minimum transmission is approximately 50% because these cholesteric materials reflect only one polarization direction. Below 400 nm the transmission drops to zero due to absorption by the mesogenic group. Figure 4 shows the dependence of the reflection wavelength on the temperature of this mixture. A strong thermochromic effect was measured between 75 and 80°C; this might be attributed to a nearby transition to the smectic phase. Smectic phases have a strong tendency to unwind the cholesteric helix and thus reduce the HTP, an effect not uncommon in these types of diacrylates [20]. Table 3 shows thermal measurements of this mixture. A smectic transition was indeed observed at 69°C, which is probably responsible for the sharp increase in wavelength observed.

Upon irradiation for 30 min a decrease in reflection wavelength was observed at temperatures below 80°C; this was unexpected, i.e. a decrease in HTP. After longer irradiation (90 min) the reflection wavelength stopped changing. At temperatures above 80°C almost no change was observed but below this temperature the HTP had increased again. After irradiation, the smectic transition could not be observed above 40°C, the temperature at which phase separation due to crystallization of one of

Table 3. Liquid crystalline transition temperatures of two mixtures of **2**, **3** and **5**, before and after irradiation at 365 nm.

Components	State	Phase transitions/°C
3 (50%) and **5** (50%)	Before irradiation	SmA–69–N*–116–I
3 (50%) and **5** (50%)	After irradiation	N*–104–I
2 (20%), **3** (60%) and **5** (20%)	Before irradiation	N*–108–I
2 (20%), **3** (60%) and **5** (20%)	After irradiation	N*–97–I

the components occurred. Thus, lowering the transition temperature due to the *E–Z* isomerisation of **5** results in a higher HTP. This is due to a lower ordering in the system because the *Z* isomer has a lower aspect ratio than the *E* isomer. This effect is also apparent from a comparison of the temperatures of transition to the isotropic phase, presented in table 3, which is found at lower temperatures after irradiation. It could be concluded that the effect of the smectic–cholesteric phase transition plays a dominant role in the HTP in this system.

In order to suppress the smectic properties of the cholesteric mixture, **5** was replaced by a 1:1 mixture of **2** and **5**. Compound **2** does not exhibit smectic behavior (see table 1). Table 3 shows that this mixture did not exhibit a smectic phase. Below 40°C phase separation occurred, resulting in a sample that scatters. Due to the higher content of the non-chiral component **3**, the reflection wavelength was observed in the green region as shown in figure 5. The same figure shows that the thermochromic effect is much smaller and opposite to that observed for the 1:1 mixture of **3** and **5**. Mixtures of non-smectic compounds containing **1** and **3** or similar compounds exhibit a stronger thermochromic effect [11]. The smectic nature of **5** probably still has a strong effect on the behaviour of this cholesteric mixture. Upon irradiation of this mixture, a small increase in the reflection wavelength was observed below 70°C. Because this effect is only a few nm, it is not very interesting for practical applications. Table 3 shows a decrease of about 11°C in the isotropic transition temperature of the mixture after irradiation. Although we were unable to determine the extent of *E–Z* isomerisation in the cells, it seems that by changing the medium by photoisomerization, the HTP of **5** increases. The HTP of its *Z* isomer, which is needed to analyse this effect, was not determined.

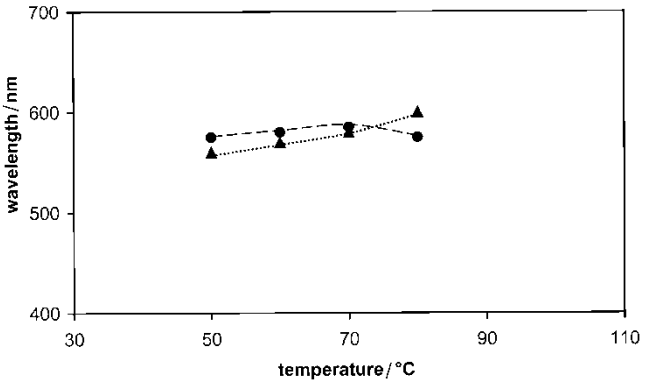


Figure 5. Transmission spectra of a 5 μm cell filled with a 2:6:2 mixture of **2, 3** and **5** before irradiation (▲) and after irradiation for 90 min (●) at 365 nm.

The dependence of the HTP on the kind of liquid crystalline mixture is not an uncommon effect [17].

In the two mixtures that were studied, the smectic behaviour of compound **5** determines the effect of the chemical isomerization on the helical twisting power. The experiments in E7, which is a nematic medium, show that the HTP change upon isomerization seems promising; however, in that system the low concentration of **5** (less than 2 wt %) has no effect on the phase behaviour. If the concentration is increased to obtain materials which reflect visible light, the smectic nature of **5** starts to play an important role. Although the colour changes obtained in the experiment with the mixture of **3** and **5** cover the whole visible spectrum, the strong temperature dependence of the mixture before and after irradiation makes the material less suitable for practical applications. This is especially the case if the colours made by irradiation are stabilized by thermal polymerization. Heating the acrylate samples to initiate polymerization would have a strong and poorly controllable effect on the reflection wavelength.

4. Conclusions and outlook

Due to photodecomposition, chiral compounds in which the mesogenic group was derived from 4-(4-hydroxybenzoyloxy)-4′-hydroxystilbene were unsuitable as *E–Z* isomerizable compounds. Isomers derived from 4-(4-hydroxyphenoxycarbonyl)-4′-hydroxystilbene show a clean *E–Z* isomerization. The HTP of the chiral diacrylate derived from the latter mesogenic group changes from 7 to 3 μm^{-1} in dilute nematic solution. Colour changes of cholesteric material containing this compound were observed. The effect was very dependent on temperature and concentration due to the strong smectic character of this diacrylate. In order to use these types of stilbene compound as chiral isomerizable compounds, their smectic nature should be suppressed. This can be done by introducing substituents in the aromatic rings. Another possibility is to change the nature of the chiral moieties in order to obtain a higher HTP. This would enable a lower concentration of the compounds to be used, thus preventing the strong 'smectic' phase effect on the mixtures and work on such compounds is in progress.

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