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Photoisomerizable chiral compounds derived from isosorbide and cinnamic acid

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Photoisomerizable chiral compounds derived from isosorbide and cinnamic acid

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The syntheses of derivatives of isosorbide and cinnamic acid are described. These chiral compounds are photoisomerizable. The *Z*-isomers could also be obtained after irradiation of these *E*-isomeric cinnamic derivatives. The *Z*-isomers were found to have a much lower helical twisting power than the *E*-isomers. These compounds are very suitable for use in cholesteric colour filters for liquid crystal displays. This was investigated by functionalizing the *E*-isomeric derivatives with two acrylate groups. The reflection wavelength of cholesteric layers made with these diacrylates can be tuned by means of UV irradiation because the pitch of the cholesteric layer increases on isomerization to the *Z*-isomer. Subsequent photopolymerization results in cholesteric films with excellent thermal stability.

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1. Introduction

Cholesteric liquid crystalline materials have received much attention due to their capability of reflecting circularly polarized light. The development of photoisomerizable chiral molecules in particular has received much interest [1]. Such materials find application in the production of cholesteric colour filters for use in liquid crystal displays because of the UV light-induced colour change. The menthone derivative **1b** (figure 1) is an example of a molecule that can be used for the colour change by means of *E–Z* photoisomerization. The reflection wavelength (λ) of a cholesteric layer containing **1b** is defined by [2]:

$$\lambda = np = n(HTP_E\ x_E + HTP_Z\ x_Z)^{-1} \qquad (1)$$

where n is the mean refractive index of the cholesteric mixture, p is the pitch of the helix of the cholesteric structure, x_E is the weight fraction of **1b** (the *E*-isomer) present in the cholesteric mixture and x_Z is the weight fraction of photoisomerized material (*Z*-isomer, obtained through photoisomerization of **1b**); HTP_E is the so-called helical twisting power, which is a property of **1b**, namely the reciprocal of the pitch of the helix for $x_E=1$, and HTP_Z is the helical twisting power of the *Z*-isomer of **1b**. The change in conformation upon *E–Z* photoisomerisation of **1b** causes the reflection wavelength to increase, as the HTP_E of this compound is approximately $19\,\mu m^{-1}$, while HTP_Z is approximately $3\,\mu m^{-1}$ [3].

To produce cholesteric colour filters, compound **1b** was added to a mixture of nematic diacrylates and a photoinitiator [4, 5]. When the mixture was coated on a rubbed alignment layer a blue reflecting film was formed. The photoisomerization reaction was effected in a single UV irradiation step with the aid of a pixelated mask, the pixels having 100%, 0% and intermediate transmission, leading to the red, blue and green pixels, respectively [4, 6]. Use of the correct irradiation dose for the green and red pixels optimizes the colours. Subsequent photopolymerization of the film containing the pixelated reflection colours led to the formation of a stable crosslinked material. The process conditions were chosen so that the two photochemical processes, i.e. isomerization and polymerization, would not interfere [4]. Photopolymerization will not start if air is present due to the inhibitive effect of oxygen on the acrylate polymerization reaction. The combination of this effect and the relatively low UV intensity needed for isomerization results in easy formation of the colours in air without noticeable polymerization. The photopolymerisation reaction was effected in an inert atmosphere (nitrogen or argon), in which it proceeded at a much higher rate than the isomerization process. This led to rapid fixation of the patterned cholesteric structure without changes in its optical properties. The crosslinking resulted in a material that is stable against UV light and at elevated temperatures. These cholesteric colour filters reflect colours of high colour purity and are interesting materials for new generations of liquid crystal displays [7, 8].

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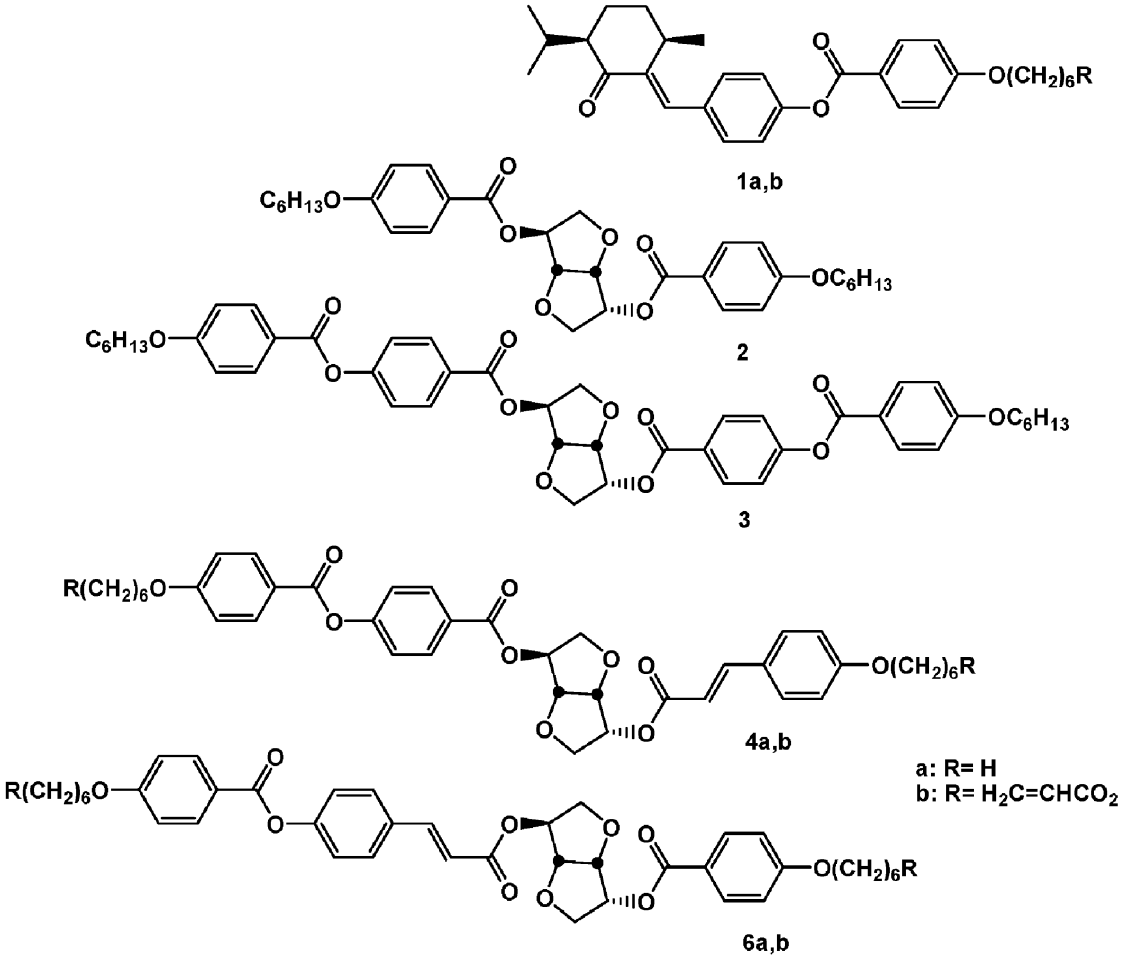

Figure 1. Structures of the chiral compounds discussed in the text.

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However, the manufacture of LCDs imposes more severe demands on the stability of the cholesteric colour filter, as it involves high temperature treatments (typically 200°C) such as ITO deposition directly on the colour filter followed by the application and baking of a polyimide film on top of the ITO. During these processes degradation of the filters was observed. This degradation is partly attributable to the thermal instability of the menthone-derived chiral moiety and partly to the fact that this chiral compound is a monoacrylate, and hence leads to the formation of polymer networks with a relatively low crosslink density upon photopolymerisation [9, 10]. In previous publications in this journal we reported several alternative structures for compound **1a**, in which the menthone moiety was replaced by various derivatives of cyclohexanone [11–13]. That previous research led to a better understanding of the structure–property relationship of these chiral materials, but most of them are rather difficult to synthesize, or exhibit *HTP* values that are too low for these materials to be used in colour filter manufacturing. We therefore searched for other structures exhibiting higher *HTP* values so that smaller amounts of chiral compound could be used. This is favourable if the chiral moiety is the most unstable structure in the cholesteric colour filter, as is the case with the menthone derivative **1b** [9]. It would moreover be advantageous if it were to be possible to functionalize these new compounds with two acrylate groups in order to increase the crosslink density of the cholesteric colour filters. This could lead to greater thermal stability.

Diesters of isosorbide such as **2** and **3** (figure 1) are compounds with relatively high *HTP* values, as shown in table 1 [14]. Compounds containing two acrylate groups with these structures can be prepared relatively easily. Cholesteric mixtures prepared with these polymerizable compounds form very stable polymeric networks after photopolymerisation [15].

Table 1. Physical properties of isosorbide derivatives **2**, **3** [14]. Physical properties of the menthone derivatives **1a** and **1b** [3] and of the isosorbide derivatives **4a, 4b, 5a, 6a, 6b** and **7a** before and after irradiation with a TL-08 lamp.

Compound	M.p. °C	*HTP* μm^{-1} in E7	HTP_{pss} μm^{-1} in E7[a]	Conversion % calculated from HTP_{pss}[b]	Conversion % measured from UV spectra
1a	101	−19	−3		
1b	76	−20	−2		
2	91	47	–		
3	145	66	–		
4a	107	56	6	78	81
4b	62	42	19		
5a	73	−8	8	25	18
6a	163	54	23	50	61
6b	129	38	13		
7a	90	−8	20	48	38

[a]Defined as the reciprocal of the product of the pitch and the initial amount of *E*-isomers; see equation (2).
[b]According to equation (3).

Isosorbide esterified by 4-methoxycinnamic acid changes its *HTP* as a result of *E–Z* isomerization during irradiation. This compound has proven to be of interest in complex chiral mixtures to increase or decrease the *HTP* upon irradiation [16–18]. Theoretical calculations predict a large difference in *HTP* values of the isomers of such cinnamic acid derivatives, and hence a large change in pitch upon *E–Z* isomerization [19]. In order to study the suitability of such structures for use in cholesteric colour filters, it was decided to synthesize and investigate the properties of model compounds **4a** and **6a** (figure 1). In these structures ester groups derived from cinnamic acid replace one of the ester groups derived from benzoic acid in compounds **3** and **2**, respectively. Compounds **5a** and **7a**, which are the *Z*-isomers of **4a** and **6a**, respectively, have also been prepared and characterized. The properties of these compounds will be compared with those of model compound **1a**. Furthermore, the polymerizable analogues of **4a** and **6a**, the diacrylates **4b** and **6b**, respectively, were prepared. These molecules are suitable for replacing menthone derivative **1b** in cholesteric mixtures. Some properties of cholesteric films made with these new diacrylates will be presented.

2. Experimental

2.1. *Materials and methods*

Procedures described in the literature were used to obtain 4-(6-acryloyloxyhexyloxy)benzoic acid (**8b**) [20], 4-hexyloxycinnamic acid (**17a**) [21], 4-(6-acryloyloxyhexyloxy)cinnamic acid (**17b**) [21] and methyl 4-hydroxycinnamate (**18**) [22].

E7 (a mixture of nematic liquid crystals derived from cyanobiphenyl), S811 ((*S*)-1-methylheptyl 4-(4-hexyloxybenzoyloxy)benzoate), RM82 {(4-(6-acryloyloxyhexyloxy)benzoyloxy)-2-methylphenyl 4-(6-acryloyloxyhexyloxy)benzoate} and RM257 {(4-(3-acryloyloxypropyloxy)benzoyloxy)-2-methylphenyl 4-(3-acryloyloxypropyloxy)benzoate} were obtained from Merck. Darocur® 4265 photoinitiator was obtained from Ciba Geigy. All the other chemicals were obtained from Aldrich.

Absorption UV spectra were recorded in acetonitrile solution using a Unicam UV2-100 spectrometer. Transmission spectra of the cholesteric films were recorded using a Perkin-Elmer spectrometer, equipped with a combination of a linear polarizer and an achromatic $\lambda/4$ film to generate circularly polarized light the handedness depending on the angle between the optical axes of the two components. The reflection was measured as transmission loss.

NMR spectra were recorded with a Bruker DPX300 spectrometer in a deuteriated dichloromethane or deuteriated chloroform solution. The ^{1}H and ^{13}C NMR data were fully consistent with the required structures and confirmed the purity of all the final products. The spectra were interpreted with the aid of 2D ^{13}C–^{1}H correlation spectra.

FTIR spectra were recorded on an ATI Mattson Genesis II spectrometer. Maldi-TOF mass spectra were recorded on a Voyager-De Pro machine using α-cyano-4-hydroxycinnamic acid as the matrix.

The helical twisting power was determined using the Grandjean–Cano method [23]. Wedge cells (EHC Japan, $\tan\alpha = 0.0083$) were filled with solutions of one of the chiral compounds in E7 and solutions of these compounds with S811 in E7 (in order to determine the sign of the *HTP*). The total amount of chiral compounds never exceeded 1 wt%. The clearing point of these mixtures before and after irradiation differed less than 1°C from the clearing point of pure E7. Irradiation was performed with a TL08 light source (Philips, broad spectrum around $\lambda = 350$ nm,

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I=0.8 mW cm^{-2}), a PL10 light source (Philips, λ_{max}=365 nm, I=3.8 mW cm^{-2}) or a HPA light source (Philips, broad spectrum, I=4.0 mW cm^{-2}). The distance between the disclination lines was measured before and after irradiation.

2.2. *Synthesis*

The various syntheses were carried out as indicated in schemes 1 and 2.

2.2.1. Ethoxymethyl 4-hydroxybenzoate (9). 24.5 ml (0.26 mol) of chloromethyl ethyl ether in 100 ml of dichloromethane was added dropwise to a solution of 36.7 ml (0.26 mol) of triethylamine and 36.1 g (0.26 mol) of 4-hydroxybenzoic acid in 200 ml of dichloromethane cooled in an ice/water bath. After the mixture had been stirred for 2 h it was extracted once with 150 ml of water, then with 150 ml of 0.25M HCl and finally with 150 ml of a saturated sodium bicarbonate solution. The solvent was evaporated. The remaining oil was dissolved in 500 ml of diethyl ether and extracted once with 250 ml of water, once with 250 ml of a saturated sodium bicarbonate solution, and finally with 250 ml of brine. The organic layer was dried over magnesium sulphate and subjected to evaporation. 42.2 g of a clear oil (77%) was obtained that crystallized as white crystals.

2.2.2. Ethoxymethyl 4-(4-hexyloxybenzoyloxy)benzoate (10a). 41.15 g (0.2 mol) of *N*,*N*-dicyclohexyl carbodiimide (DCC) was added to a solution of 42.2 g (0.20 mol) of compound **9**, 44.6 g (0.2 mol) of 4-hexyloxybenzoic acid (**8a**) and 2.4 g (0.02 mol) of 4-*N*,*N*-dimethylaminopyridine (DMAP) in 500 ml of dichloromethane cooled in an ice/water bath. The mixture was filtered through a thin silica layer and subjected to evaporation after stirring at room temperature under nitrogen for one night. 75 g of the product (88%) was obtained as a white powder after recrystallization from methanol.

2.2.3. Ethoxymethyl 4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoate (10b). This compound was prepared in a 90% yield in the same manner as described for compound **10a**, substituting 4-hexyloxybenzoic acid (**8a**) by 4-(6-acryloyloxyhexyloxy)benzoic acid (**8b**).

2.2.4. 4-(4-Hexyloxybenzoyloxy)benzoic acid (11a). A mixture of 75 g (0.18 mol) of compound **10a**, 5.0 g (0.02 mol) of pyridinium 4-toluenesulphonate and 400 ml of EtOH was heated at 60°C for 15 h. After cooling to room temperature the product crystallized. It was collected, washed with 300 ml of ethanol and dried in a desiccator. 48 g of a white powder (67 %) was obtained.

2.2.5. 4-[4-(6-Acryloyloxyhexyloxy)benzoyloxy]benzoic acid (11b). This compound was prepared in a 70% yield in the same manner as described for compound **11a**, starting from compound **10b**.

2.2.6. (3*S*,3a*R*,6*R*,6a*R*)-3-acetoxyhexahydrofuro[3,2-b]furan-6-ol (12) [24, 25]. A mixture of 292 g (2 mol) of isosorbide, 112 ml (2.0 mol) of acetic acid, 2.0 g (10.4 mmol) of 4-toluenesulphonic acid and 700 ml of toluene was heated at reflux for 6 h with constant removal of water (Dean–Stark device); the solvent was then evaporated. 4 g of potassium carbonate was added and the mixture was heated at 150°C for 1 h followed by fractionation at reduced pressure. The fraction collected at about 110°C/0.4 mbar was crystallised three times from isopropanol at 0°C and dried in a desiccator. 137 g of the product (yield 37%) was obtained as white crystals with m.p.=78°C.

2.2.7. (3*S*,3a*R*,6*R*,6a*R*)-6-(tetrahydro-2H-pyran-2-yloxy)hexahydrofuro[3,2-b]furan-3-yl acetate (13). 100 ml (1.09 mol) of 3,4-dihydro-2H-pyran was added dropwise to a solution of 9.14 g (36.4 mmol) of pyridinium 4-toluenesulphonate and 137 g (0.73 mol) of compound **12** in 650 ml of dichloromethane under a nitrogen atmosphere. The solution was stirred overnight. The mixture was extracted twice with water and twice with an aqueous sodium bicarbonate solution (5%). The organic layer was dried over magnesium sulphate and filtered through a pad of silica, after which the solvent was evaporated to leave 194 g of a clear oil (yield 98%).

2.2.8. (3*S*,3a*R*,6*R*,6a*R*)-6-(tetrahydro-2H-pyran-2-yloxy)hexahydrofuro[3,2-b]furan-3-ol (14). A mixture of 194 g (0.71 mol) of compound **13**, 31 g (0.77 mol) of NaOH, 40 ml of water and 450 ml of MeOH was heated at reflux for 1 h. After evaporation at reduced pressure, 800 ml of dichloromethane and 800 ml of brine were added to the residue. After separation, the aqueous layer was extracted with 500 ml of dichloromethane. The combined organic layers were dried over magnesium sulphate and the solvent was evaporated to leave 154 g of a yellow viscous oil (yield 94%).

2.2.9. (3*S*,3a*R*,6*R*,6a*R*)-6-(tetrahydro-2H-pyran-2-yloxy)hexahydrofuro[3,2-b]furan-3-yl 4-(4-hexyloxybenzoyloxy)benzoate (15a). 8.25 g (0.04 mol) of DCC was added to a mixture of 13.7 g (0.04 mol) of compound **11a**, 9.21 g (0.04 mol) of compound **14**, 0.49 g (4 mmol)

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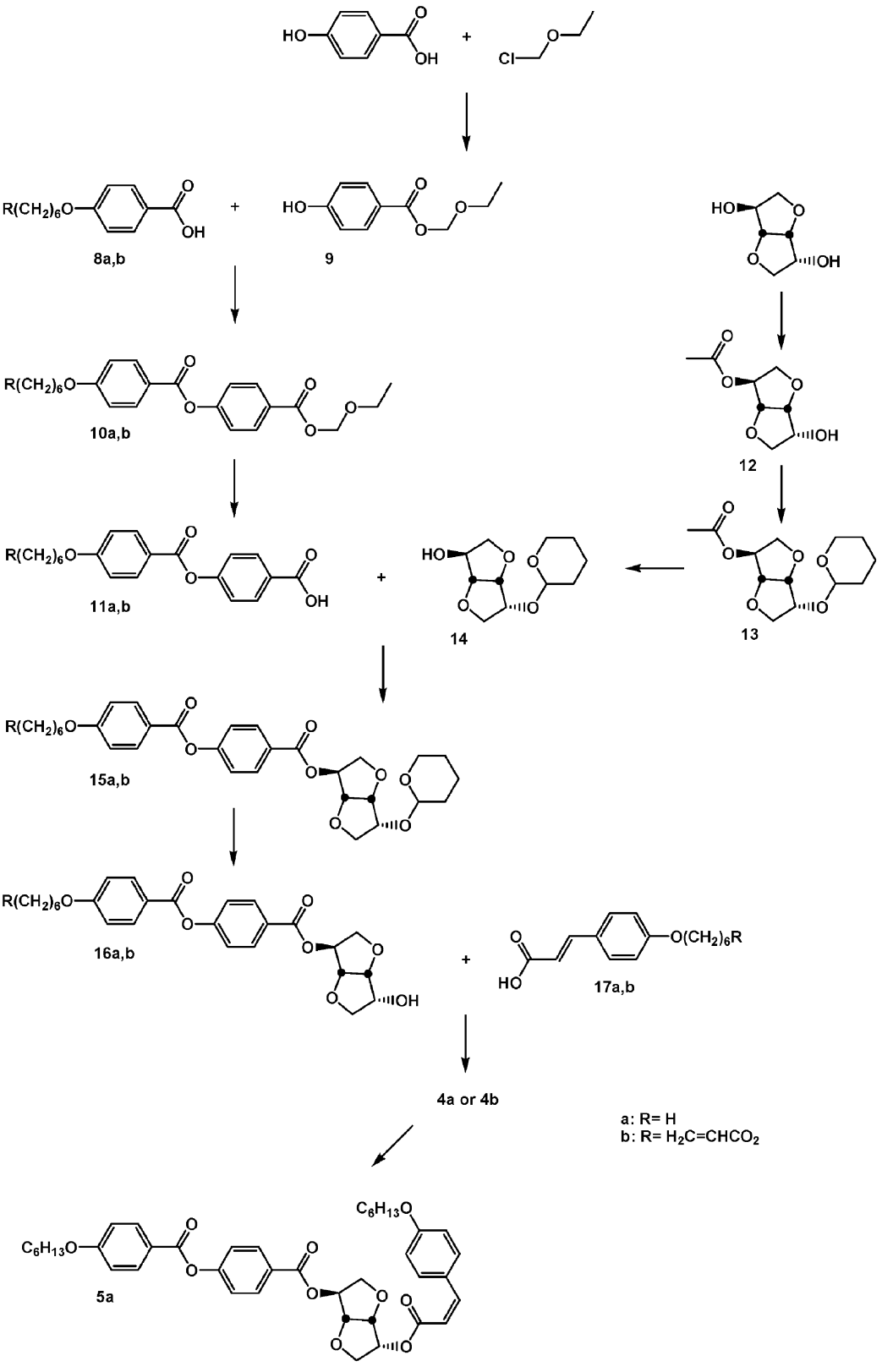

Scheme 1. Synthesis of compounds **4a**, **4b** and **5a**.

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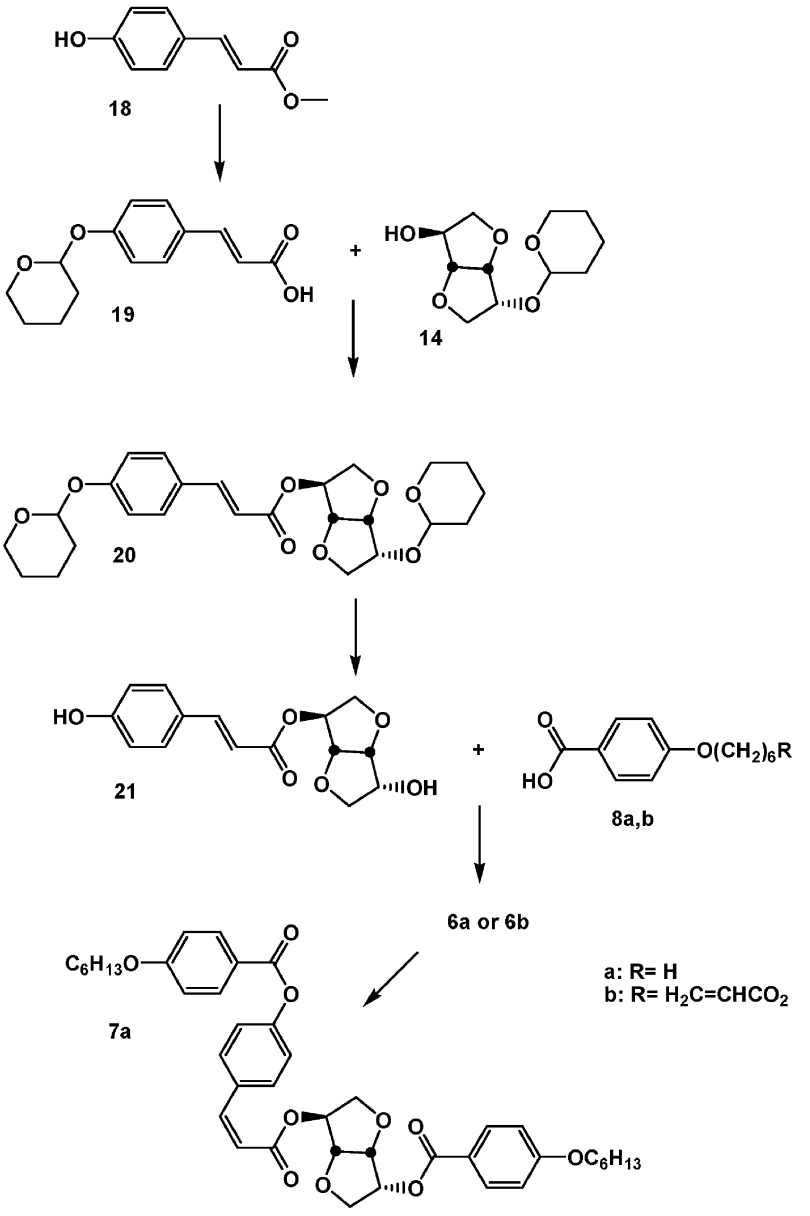

Scheme 2. Synthesis of compounds **6a**, **6b** and **7a**.

of DMAP and 100 ml of dichloromethane stirred under nitrogen in an ice/water bath. After stirring for one night at room temperature. It was filtered through silica and evaporated to give 21.6 g (97%) of the product as an oil, which was used without further purification in the next reaction step.

2.2.10. (3*S*,3a*R*,6*R*,6a*R*)-6-(tetrahydro-2H-pyran-2-yloxy)hexahydrofuro[3,2-b]furan-3-yl 4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoate (15b). This compound was prepared in a 90% yield in the same manner as described for compound **15a**, starting from compound **11b**.

2.2.11. (3*S*,3a*R*,6*R*,6a*R*)-3-[4-(4-hexyloxybenzoyloxy)benzoyloxy]hexahydrofuro[3,2-b]furan-6-ol (16a). A mixture of 20.04 g (36 mmol) of compound **15a**, 0.90 g (3.6 mmol, 10 mol%) of pyridinium 4-toluenesulphonate and 100 ml of ethanol was heated for 5 h at 55°C. After cooling the product crystallized. It was filtered, washed with cold ethanol and dried at 60°C in vacuum; 15.3 g (90%) of a white solid was obtained.

2.2.12. (3*S*,3a*R*,6*R*,6a*R*)-3-{4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}hexahydrofuro[3,2-b]furan-6-ol (16b). This compound was prepared in 73% yield in

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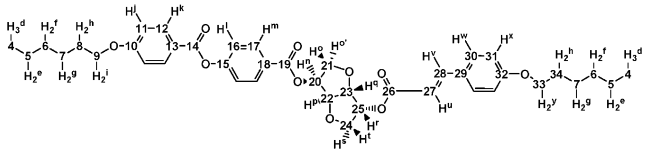
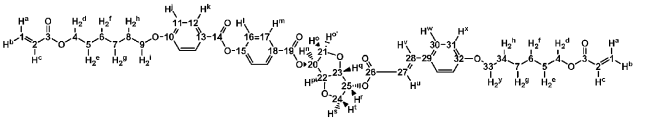
the same manner as described for compound **16a**, starting from compound **15b**.

2.2.13. (3*S*,3a*R*,6*R*,6a*R*)-3-[4-(4-hexyloxybenzoyloxy) benzoyloxy]hexahydrofuro[3,2-b]furan-6-yl 4-hexyloxycinnamate (4a). 3.10 g (15 mmol) of DCC was added to a mixture of 7.1 g (15 mmol) of compound **16a**, 3.7 g (15 mmol) 4-hexyloxycinnamic acid (**17a**), 0.18 g (1.5 mmol) of DMAP and 50 ml of dichloromethane cooled in an ice/water bath. After the reaction mixture had been stirred for one night at room temperature it was filtered through silica and evaporated. 7.8 g (74%) of the product was obtained after recrystallization from a 3:1 mixture of ethanol and dichloromethane at −20°C. IR (chloroform solution, in cm^{-1}): 2956 (CH_3), 2929 (CH_2), 1740 (C=O, benzoate), 1719 (C=O, cinnamate), 1635 (C=C), 1605 and 1512 (aromatic rings). MS (MALDI): calculated for $C_{41}H_{48}O_{10}$ 700.32, found 700.39. ^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.14 (d, 2H, J=9.0, H^k), 8.10 (d, 2H, J=9.0, H^m), 7.70 (d, 1H, J=16.2, H^v), 7.48 (d, 2H, J=8.7, H^w), 7.30 (d, 2H, J=9.0, H^l), 6.97 (d, 2H, J=9.0, H^j), 6.90 (d, 2H, J=8.7, H^x), 6.39 (d, 1H, J=16.2, H^u), 5.48 (d, 1H, J=1.9, H^n), 5.31 (q, 1H, J=5.2, H^r), 4.99 (t, 1H, J=5.2, H^q), 4.68 (d, 1H, J=5.2, H^p), 4.15 (m, 2H, H^o and $H^{o'}$), 4.08 (dd, 1H, J_1=9.9, J_2=5.2, H^t), 4.05 (t, 2H, J=6.4, H^i), 3.99 (t, 2H, J=6.4, H^y), 3.92 (dd, 1H, J_1=9.9, J_2=5.2, H^s), 1.82 (q, 4H, J=6.4, H^h), 1.47 (q, 4H, J=6.4, H^e), 1.38 (m, 8H, H^f+H^g), 0.91 (t, 6H, J=6.4, H^d).



^{13}C NMR (δ in ppm, relative to TMS): 167.1 (C^{26}), 165.3 (C^{19}), 164.7 (C^{14}), 164.2 (C^{10}), 161.6 (C^{32}), 155.6 (C^{15}), 146.1 (C^{28}), 132.8 (C^{12}), 131.7 (C^{17}), 130.4 (C^{30}), 127.1 (C^{18}), 127.3 (C^{29}), 122.4 (C^{16}), 121.3 (C^{13}), 115.1 (C^{27}), 114.8 (C^{11}+C^{31}), 86.4 (C^{22}), 81.6 (C^{23}), 79.0 (C^{20}), 74.4 (C^{25}), 74.0 (C^{21}), 70.7 (C^{24}), 68.8 (C^9), 68.6 (C^{33}), 32.0 (C^6), 29.5 (C^8+C^{34}), 22.8 (C^5), 26.0 (C^7), 14.4 (C^4).

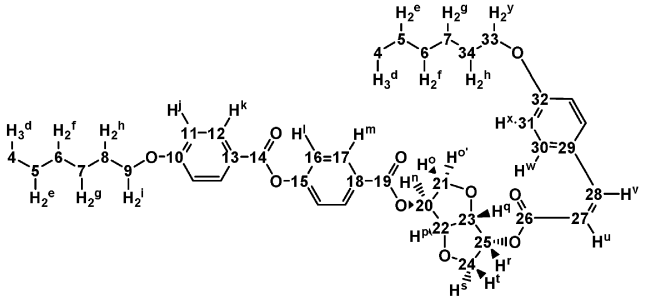
2.2.14. (3*S*,3a*R*,6*R*,6a*R*)-3-{4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}hexahydrofuro[3,2-b]furan-6-yl 4-(6-acryloyloxyhexyloxy)cinnamate (4b). This compound was prepared in 70% yield in the same manner as described for compound **4a**, starting from 4-(6-acryloyloxyhexyloxy)cinnamic acid (**17b**) and compound **16b**. IR (chloroform solution, in cm^{-1}): 2944 (CH_2), 1727 (C=O, benzoate, cinnamate, acrylate), 1636 (C=C), 1605 and 1511 (aromatic rings), 1408 (CH_2–acrylate), 984 and 976 (CH=CH_2). MS (MALDI): calculated for $C_{47}H_{52}O_{14}$ 840.34, found 840.35. ^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.14 (d, 2H, J=9.0, H^k), 8.10 (d, 2H, J=9.0, H^m), 7.70 (d, 1H, J=16.2, H^v), 7.48 (d, 2H, J=8.7, H^w), 7.30 (d, 2H, J=9.0, H^l), 6.97 (d, 2H, J=9.0, H^j), 6.90 (d, 2H, J=8.7, H^x), 6.42 (dd, 2H, J_1=17.3, J_2=1.5, H^a), 6.39 (d, 1H, J=16.2, H^u), 6.13 (dd, 2H, J_1=17.3, J_2=10.5, H^c), 5.82 (dd, 2H, J_1=10.5, J_2=1.5, H^b), 5.48 (d, 1H, J=1.9, H^n), 5.31 (q, 1H, J=5.2, H^r), 4.99 (t, 1H, J=5.2, H^q), 4.68 (d, 1H, J=5.2, H^p), 4.18 (t, 4H, J=6.4, H^d), 4.15 (m, 2H, H^o and $H^{o'}$), 4.08 (dd, 1H, J_1=9.9, J_2=5.2, H^t), 4.05 (t, 2H, J=6.4, H^i), 3.99 (t, 2H, J=6.4, H^y), 3.92 (dd, 1H, J_1=9.9, J_2=5.2, H^s), 1.82 (q, 4H, J=6.4, H^h), 1.72 (q, 4H, J=6.4, H^e), 1.49 (m, 8H, H^f+H^g).



^{13}C NMR (δ in ppm, relative to TMS): 166.7 (C^3), 167.1 (C^{26}), 165.3 (C^{19}), 164.7 (C^{14}), 164.1 (C^{10}), 161.6 (C^{32}), 155.6 (C^{15}), 146.1 (C^{28}), 132.8 (C^{12}), 131.7 (C^{17}), 131.0 (C^1), 130.4 (C^{30}), 129.0 (C^2), 127.2 (C^{18}), 127.3 (C^{29}), 122.4 (C^{16}), 121.5 (C^{13}), 115.1 (C^{27}), 114.8 (C^{11}+C^{31}), 86.4 (C^{22}), 81.6 (C^{23}), 79.0 (C^{20}), 74.4 (C^{25}), 74.0 (C^{21}), 70.7 (C^{24}), 68.5 (C^9), 68.3 (C^{33}), 64.9 (C^4), 29.4 (C^8+C^{34}), 28.9 (C^5), 26.1 (C^6+C^7).

2.2.15. (*Z*)-(3*S*,3a*R*,6*R*,6a*R*)-3-[4-(4-hexyloxybenzoyloxy)benzoyloxy]hexahydrofuro[3,2-b]furan-6-yl 3-(4-hexyloxphenyl)acrylate (5a). A solution of 0.5 g of compound **4a** in 10 ml of dichloromethane was irradiated with a 350 nm light source (TL-08) for 24 h. After evaporation, the isomers were separated by means of column chromatography (silica/dichloromethane). 50 mg of the product (10%) was collected as a white powder after the addition of 10 ml of ethanol to the oil obtained after the chromatography to initiate solidification. IR (chloroform solution, in cm^{-1}): 2957 (CH_3), 2933 (CH_2), 1739 (C=O, benzoate), 1730 (C=O, isomerized cinnamate), 1604 and 1511 (aromatic rings). MS (MALDI): calculated for $C_{41}H_{48}O_{10}$ 700.32, found 700.35. ^{1}H NMR (δ in ppm, relative to TMS, J in Hz): (d, 2H, J=9.0, H^k), 8.10 (d, 2H, J=9.0, H^m), 6.92 (d, 1H, J=16.2, H^v), 7.73 (d, 2H, J=8.7, H^w), 7.30 (d, 2H, J=9.0, H^l), 6.98 (d, 2H, J=9.0, H^j), 6.87 (d, 2H, J=8.7, H^x), 5.89 (d, 1H, J=16.2, H^u), 5.46 (d, 1H, J=1.9, H^n), 5.23 (q, 1H, J=5.2, H^r), 4.98 (t, 1H, J=5.2, H^q), 4.66 (d, 1H, J=5.2, H^p), 4.12 (m, 2H, H^o and $H^{o'}$), 4.02 (dd, 1H, J_1=9.9, J_2=5.2, H^t), 4.05 (t, 2H, J=6.4, H^i), 3.99 (t, 2H,

J=6.4, H^y), 3.87 (dd, 1H, J_1=9.9, J_2=5.2, H^s), 1.82 (q, 4H, J=6.4, H^h), 1.47 (q, 4H, J=6.4, H^e), 1.38 (m, 8H, H^f+H^g), 0.91 (t, 6H, J=6.4, H^d).

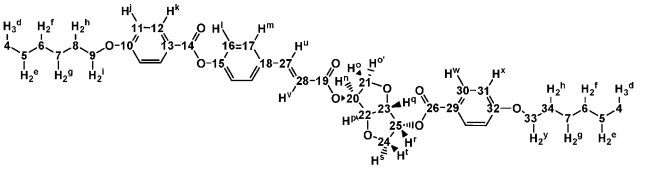


^{13}C NMR (δ in ppm, relative to TMS): 165.9 (C^{26}), 165.3 (C^{19}), 164.7 (C^{14}), 164.2 (C^{10}), 160.7 (C^{32}), 155.2 (C^{15}), 145.6 (C^{28}), 132.8 (C^{12}), 131.7 (C^{17}), 132.9 (C^{30}), 127.3 (C^{18}), 127.2 (C^{29}), 122.4 (C^{16}), 121.3 (C^{13}), 115.9 (C^{31}), 114.3 (C^{27}), 114.8 (C^{11}), 86.4 (C^{22}), 81.4 (C^{23}), 79.0 (C^{20}), 74.2 (C^{25}), 74.0 (C^{21}), 70.7 (C^{24}), 68.8 (C^9), 68.4 (C^{33}), 32.0 (C^6), 29.5 (C^8+C^{34}), 22.8 (C^5), 26.0 (C^7), 14.4 (C^4).

2.2.16. 4-(tetrahydro-2H-pyran-2-yloxy)cinnamic acid (19). 14 ml of 3,4-dihydropyran (150 mmol) was added dropwise to a mixture of 17.8 g of methyl 4-hydroxycinnamate (100 mmol), 0.34 g of 4-toluenesulphonic acid (2 mmol) and 250 ml of diethyl ether. After the mixture had been stirred for an hour it was extracted with, successively, 200 ml of a 5% sodium hydroxide solution and 200 ml of brine, then evaporated. The remaining solid was mixed with 50 ml of ethanol and 50 ml of an aqueous solution of 8 g of potassium hydroxide. After heating at reflux for 2 h, 150 g of ice was added followed by dropwise addition of 2.5N hydrochloric acid to bring the pH to 4. The precipitated solid was filtered off and washed with water; 19.6 g (79%) of a white powder was obtained after drying in a desiccator over silica.

2.2.17. (3*S*,3a*R*,6*R*,6a*R*)-3-(4-hydroxy)cinnamoyloxy) hexahydrofuro[3,2-b]furan-6-ol (21). 4.1 g of DCC (20 mmol) was added to a mixture of 4.9 g of compound **19** (20 mmol), 4.6 g of compound **14** (20 mmol), 0.24 g of DMAP (2 mmol) and 50 ml of dichloromethane cooled in an ice/water bath. After the mixture had been stirred overnight at room temperature it was filtered through silica and evaporated. The crude intermediate (3*S*,3a*R*,6*R*,6a*R*)-6-(tetrahydro-2H-pyran-2-yloxy)hexahydrofuro[3,2-b]furan-3-yl 4-(-tetrahydro-2H-pyran-2-yloxy) cinnamate (**20**) obtained as an oil was mixed with 0.48 g of pyridinium 4-toluenesulphonate (1.9 mmol) and 60 ml of absolute ethanol and heated at 60°C for 3 h. The cooled solution was added dropwise to a mixture of 50 g of ice and 100 g of water; 3.7 g of the product (66%) was obtained after drying of the precipitate over silica in a desiccator.

2.2.18. (3*S*,3a*R*,6*R*,6a*R*)-6-(4-hexyloxybenzoyloxy) hexahydrofuro[3,2-b]furan-3-yl 4-(4-hexyloxybenzoyloxy)cinnamate (6a). 2.5 g (12 mmol) of DCC was added to a mixture of 0.14 g (1.2 mmol) of DMAP, 1.8 g (5.8 mmol) of compound **21**, 2.7 g (12.0 mmol) of 4-hexyloxybenzoic acid (**8a**) and 40 ml of dichloromethane cooled in an ice-bath. After stirring for one night at room temperature the mixture was filtered and purified by column chromatography (silica/dichloromethane); 2.5 g of white crystals was obtained (yield 61%) after recrystallization from ethyl acetate. IR (chloroform solution, in cm^{-1}): 2960 (CH_3), 2935 (CH_2), 1730 (C=O, benzoate), 1724 (C=O, cinnamate), 1639 (C=C), 1606 and 1511 (aromatic rings). MS (MALDI): calculated for $C_{41}H_{48}O_{10}$ 700.32, found 700.28. ^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.14 (d, 2H, J=9.0, H^k), 8.02 (d, 2H, J=8.7, H^w), 7.70 (d, 1H, J=16.2, H^v), 7.58 (d, 2H, J=9.0, H^m), 7.24 (d, 2H, J=9.0, H^l), 6.97 (d, 2H, J=9.0, H^j), 6.91 (d, 2H, J=8.7, H^x), 6.40 (d, 1H, J=16.2, H^u), 5.40 (q, 1H, J=5.2, H^r), 5.37 (d, 1H, J=1.9, H^n), 5.02 (t, 1H, J=5.2, H^q), 4.62 (d, 1H, J=5.2, H^p), 4.05 (m, 8H, H^i, H^y, H^o, H^o, H^t, and H^s), 1.82 (q, 4H, J=6.4, H^h), 1.47 (q, 4H, J=6.4, H^e), 1.38 (m, 8H, H^f+H^g), 0.91 (t, 6H, J=6.4, H^d).



^{13}C NMR (δ in ppm, relative to TMS): 166.3 (C^{26}), 166.1 (C^{19}), 165.0 (C^{14}), 164.1 (C^{10}), 163.7 (C^{32}), 153.2 (C^{15}), 145.3 (C^{28}), 132.8 (C^{12}), 132.2 (C^{17}), 132.1 (C^{18}), 129.8 (C^{30}), 122.8 (C^{16}), 121.9 (C^{29}), 121.5 (C^{13}), 117.7 (C^{27}), 114.8 (C^{11}), 114.6 (C^{31}), 86.6 (C^{22}), 81.6 (C^{23}), 78.6 (C^{20}), 74.5 (C^{25}), 74.0 (C^{21}), 71.2 (C^{24}), 68.8 (C^9), 68.7 (C^{33}), 32.0 (C^6), 29.5 (C^8+C^{34}), 26.0 (C^7), 22.8 (C^5), 14.4 (C^4).

2.2.19. (3*S*,3a*R*,6*R*,6a*R*)-6-[4-(6-acryloyloxyhexyloxy) benzoyloxy]hexahydrofuro[3,2-b]furan-3-yl 4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]cinnamate (6b). This compound was prepared as a white powder in 45% yield in the same manner as described for compound **6a**, starting from 4-(6-acryloyloxyhexyloxy)benzoic acid (**8b**). IR (chloroform solution, in cm^{-1}): 2939 (CH_2), 1732 (C=O, benzoate, cinnamate, acrylate), 1635

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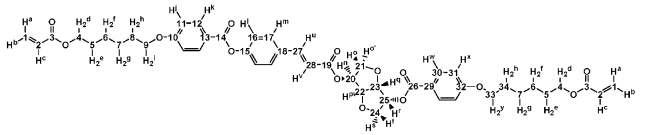
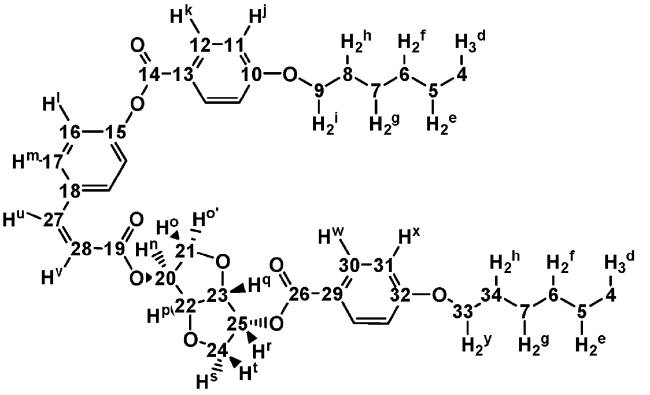
(C=C), 1604 and 1510 (aromatic rings), 1408 (CH_2–acrylate), 990 and 971 (CH=CH_2). MS (MALDI): calculated for $C_{47}H_{52}O_{14}$ 840.34, found 840.28. ^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.14 (d, 2H, J=9.0, H^k), 8.02 (d, 2H, J=8.7, H^w), 7.70 (d, 1H, J=16.2, H^v), 7.58 (d, 2H, J=9.0, H^m), 7.24 (d, 2H, J=9.0, H^l), 6.97 (d, 2H, J=9.0, H^j), 6.91 (d, 2H, J=8.7, H^x), 6.42 (dd, 2H, J_1=17.3, J_2=1.5, H^a), 6.40 (d, 1H, J=16.2, H^u), 6.13 (dd, 2H, J_1=17.3, J_2=10.5, H^c), 5.82 (dd, 2H, J_1=10.5, J_2=1.5, H^b), 5.40 (q, 1H, J=5.2, H^r), 5.37 (d, 1H, J=1.9, H^n), 5.02 (t, 1H, J=5.2, H^q), 4.62 (d, 1H, J=5.2, H^p), 4.18 (t, 4H, J=6.4, H^d), 4.05 (m, 8H, H^i, H^y, H^o, H^o, H^t, and H^s), 1.82 (q, 4H, J=6.4, H^h), 1.72 (q, 4H, J=6.4, H^e), 1.49 (m, 8H, H^f+H^g).



^{13}C NMR (δ in ppm, relative to TMS): 166.7 (C^3), 166.3 (C^{26}), 166.1 (C^{19}), 165.0 (C^{14}), 164.1 (C^{10}), 163.6 (C^{32}), 153.2 (C^{15}), 145.3 (C^{28}), 132.8 (C^{12}), 132.2 (C^{17}), 132.1 (C^{18}), 131.0 (C^1), 129.8 (C^{30}), 129.0 (C^2), 122.8 (C^{16}), 122.1 (C^{29}), 121.6 (C^{13}), 117.7 (C^{27}), 114.8 (C^{11}), 114.6 (C^{31}), 86.6 (C^{22}), 81.6 (C^{23}), 78.6 (C^{20}), 74.5 (C^{25}), 74.0 (C^{21}), 71.2 (C^{24}), 68.5 (C^9), 68.4 (C^{33}), 64.9 (C^4), 29.4 (C^8+C^{34}), 28.9 (C^5), 26.1 (C^6+C^7).

2.2.20. (*Z*)-(3*S*,3a*R*,6*R*,6a*R*)-6-(4-hexyloxybenzoyloxy)hexahydrofuro[3,2-b]furan-3-yl 3-[4-(4-hexyloxybenzoyloxy)phenyl]acrylate (7a). A solution of 0.5 g of compound **6a** in 10 ml of dichloromethane was irradiated with a 350 nm light source (TL-08) for 24 h. After evaporation, the starting product **6a** was precipitated by adding acetonitrile and removed by filtration; 95 mg of the product (19%) was obtained as a white powder after evaporation and subsequent recrystallization from ethanol. IR (chloroform solution, in cm^{-1}): 2957 (CH_3), 2933 (CH_2), 1725 (C=O, benzoate and isomerised cinnamate), 1607 and 1511 (aromatic rings). MS (MALDI): calculated for $C_{41}H_{48}O_{10}$ 700.32, found 700.36. ^{1}H NMR (δ in ppm, relative to TMS, J in Hz): 8.12 (d, 2H, J=9.0, H^k), 8.00 (d, 2H, J=8.7, H^w), 7.65 (d, 2H, J=9.0, H^m), 7.20 (d, 2H, J=9.0, H^l), 7.04 (d, 1H, J=16.2, H^v), 6.97 (d, 2H, J=9.0, H^j), 6.90 (d, 2H, J=8.7, H^x), 5.94 (d, 1H, J=16.2, H^u), 5.34 (q, 1H, J=5.2, H^r), 5.24 (d, 1H, J=1.9, H^n), 4.86 (t, 1H, J=5.2, H^q), 4.43 (d, 1H, J=5.2, H^p), 4.05 (m, 8H, H^i, H^y, H^o, H^o, H^t, and H^s), 1.82 (q, 4H, J=6.4, H^h), 1.47 (q, 4H, J=6.4, H^e), 1.38 (m, 8H, H^f+H^g), 0.91 (t, 6H, J=6.4, H^d).



^{13}C NMR (δ in ppm, relative to TMS): 166.1 (C^{26}), 165.3 (C^{19}), 165.1 (C^{14}), 164.0 (C^{10}), 163.7 (C^{32}), 152.1 (C^{15}), 144.5 (C^{28}), 132.8 (C^{18}), 132.7 (C^{12}), 132.2 (C^{17}), 131.5 (C^{30}), 122.0 (C^{29}), 121.9 (C^{16}), 121.7 (C^{13}), 119.6 (C^{27}), 114.8 (C^{11}), 114.6 (C^{31}), 86.3 (C^{22}), 81.7 (C^{23}), 78.5 (C^{20}), 74.5 (C^{25}), 73.8 (C^{21}), 71.2 (C^{24}), 68.7 (C^9), 68.6 (C^{33}), 32.0 (C^6), 29.5 (C^8+C^{34}), 26.0 (C^7), 22.8 (C^5), 14.4 (C^4).

2.3. *Cholesteric film formation*

Cholesteric layers with a thickness of about 3.5 µm were made by spincoating at 800 rpm a solution containing 43 wt% solid material in xylene onto a glass plate coated with a rubbed alignment layer. The alignment layer induces a planar orientation of the liquid crystal molecules. The solid material consisted of 8 wt% of chiral compound **4b** or **6b**, 1% of Darocur® 4265 and 91% of a 1:4 mixture of RM82 and RM 257.

The colour change of the films before polymerization was effected in air, using a Philips HPA 400S lamp that emits a broad spectrum in the near UV region. After irradiation and heating at 70°C for 1 min the film was polymerized in a nitrogen atmosphere using the same lamp. The polymerization process was completed by heating for 90 min at 150°C in a nitrogen atmosphere.

3. Results and discussion

3.1. *Synthesis of compounds 4a, 4b and 5a*

To obtain compound **4a** the two different hydroxyl groups of isosorbide had to be esterified selectively with two different acids. In order to substitute isosorbide selectively at one of the hydroxyl groups, derivative **14**, in which one of the hydroxyl groups is protected as tetrahydropyranyl ether (see scheme 1), was prepared. Such ethers are stable under various esterification conditions and deprotection can be realized without affecting ester bonds. In order to protect selectively the hydroxyl group with the *R*-configuration, isosorbide

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was first acetylated and the isomer whose hydroxyl group with the *S*-configuration was exclusively acetylated was isolated (**12** in scheme 1). Thus, compound **12** was obtained by means of a reaction between isosorbide and acetic anhydride followed by equilibration of the various products using a base. After distillation and crystallization, **12** was obtained [24, 25]. Reaction of **12** with 3,4-dihydropyran followed by hydrolysis of the acetate **13** led to the formation of **14**.

Compound **4a** was prepared through esterification of protected isosorbide **14** with acid **11a**, deprotection of compound **15a** (leading to intermediate **16a**) and esterification with acid **17a**. Acid **11a** was prepared through esterification of hydroxybenzoic acid protected as an ethoxymethyl ester (**9**) with benzoic acid derivative **8a**, followed by deprotection under the same conditions as used for deprotection of tetrahydropyranyl ethers. Diacrylate **4b** was prepared in a similar manner using acrylic compounds **8b** and **17b** instead of **8a** and **17a**, respectively.

Compound **5a**, the *Z*-isomer of **4a**, was obtained after UV irradiation of **4a** followed by chromatographic separation of the two isomers.

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3.2. *Synthesis of compounds 6a, 6b and 7a*

Compound **6a**, which also required different esterifications for the different hydroxyl groups of isosorbide, was likewise obtained using isosorbide derivative **14** (see scheme 2). Compound **14** was esterified with protected hydroxycinnamic acid **19** leading to **20**. Acid **19** was obtained through saponification of the ester obtained after reaction between methyl 4-hydroxycinnamate (**18**) and 3,4-dihydropyran. Diol **21** obtained after deprotection of **20** was esterified with two equivalents of benzoic acid derivative **8a** to form compound **6a**. Diacrylate **6b** was prepared in a similar manner using acrylic derivative **8b** instead of **8a**. Compound **7a**, the *Z*-isomer of **6a**, was obtained after UV irradiation of **6a** followed by separation of the two isomers.

3.3. *Properties of compounds 4a, 5a, 6a and 7a*

All four new compounds are crystalline powders that form isotropic phases upon melting. Compound **6a** has a higher melting point than **4a** and **3** (see table 1). The relatively stiff, long side group derived from benzoyloxycinnamic acid of compound **6a** is probably dominant and responsible for these differences. Compounds **5a** and **7a**, which are the *Z*-isomers of **4a** and **6a**, respectively, exhibit a lower melting point than these *E*-isomers. This is probably due to their bend structure. Compound **7a** has a higher melting point than its isomer **5a**. This is in accordance with the differences found for the respective *E*-isomers **4a** and **6a**, namely the dominant effect of the side group derived from benzoyloxycinnamic acid in compounds **6a** and **7a**.

Compounds **4a** and **6a** exhibit the same *HTP* value within the experimental degree of uncertainty. Comparison with menthone compound **1a** shows that **4a** and **6a** have much higher, but inverse (i.e. with inverse handedness) *HTP* values. This means that of these isosorbide compounds smaller amounts are sufficient to make cholesteric films that reflect visible light.

The length of the molecules increases in the order **2**<**4a**=**6a**<**3**. The *HTP* values measured in E7 increase in the same order; this suggests that the *HTP* values of molecules of this type increase with the total interaction length of the molecules or the length of the central aromatic part of these molecules with the nematic host. The *HTP* values of **5a** and **7a** are identical, but have opposite signs to the *HTP* values of the corresponding *E*-isomers **4a** and **6a** (i.e. the cholesteric helix has an opposite handedness). The structural differences between the isomeric compounds **4a** and **6a** and between **5a** and **7a** hence have no significant effect on the chiral interaction with the host material (E7). No helix inversion was observed in the case of the menthone model compound **1a**, but it has been observed in various other structures similar to **1a** [12, 13].

3.4. *Photochemistry of compounds 4a, 5a, 6a and 7a*

Figure 2 shows the UV absorption spectra of **4a** and **5a** in acetonitrile solution. With the aid of the extinction coefficients of these isomers, and those of the irradiation products, the conversion could be determined.

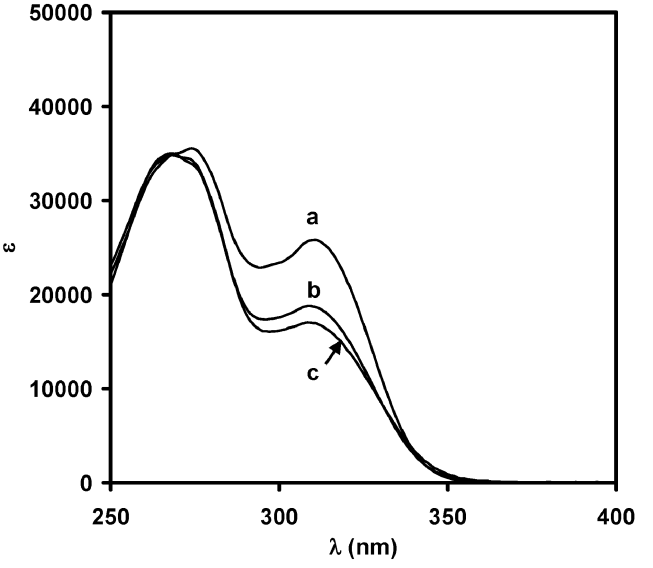

Figure 2. Absorption UV spectra of a solution of **4a** in acetonitrile (a) before and (b) after irradiation with the TL-08 lamp, and (c) of a solution of **5a** in acetonitrile.

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Irradiation of compound **4a** in acetonitrile solution with a PL-10 light source leads to a relatively slow conversion to about 20% of its isomer **5a**. This degree of conversion is much lower than that of the menthone compound **1a**, which isomerized almost completely when this light source was used. The 20% degree of conversion is insufficient to allow practical use of the compounds in colour filters because the helical pitch change will not be sufficient for the formation of all colours. Fortunately, the replacement of the irradiation source by a TL-08 lamp, which emits a broad band in the near UV region, resulted in a degree of conversion of 81% to a photostationary state (see table 1).

Figure 2 shows that at 365 nm no difference between the extinction values of **4a** and its isomer **5a** can be observed. It is possible that the absence of any difference between these extinction values was responsible for the low degree of conversion observed when the PL10 lamp was used. Such an effect was found when a derivative of camphor similar to the menthone-derived compound **1a** was irradiated [11]. Figure 2 also shows that **5a** has a lower extinction value than **4a** in the region where the TL08 lamp emits. This is probably responsible for the formation of a photostationary state that favours the formation of **5a**. The spectrum obtained upon irradiation of **5a** is nearly identical to that obtained upon irradiation of **4a** (figure 2 curve b) under the same condition with a conversion of 18% (table 1). An isosbestic point was observed at 269 nm. ^{1}H NMR spectra of irradiated **4a** or **5a** in a dichloromethane solution showed that *E*–*Z* conversion was the only process observed even after prolonged irradiation. These two observations indicate that this photoisomerization is a very clean process in which no side-products are formed.

Compounds **6a** and **7a** were insensitive to the PL-10 light source. However, upon irradiation of **6a** or **7a** with the TL-08 lamp (which emits light of lower wavelengths) in both cases a photostationary state comprising the two isomers in a ratio of approximately 4:6, respectively, was obtained (figure 3 and table 1). Figure 3 shows the UV absorption spectrum of **6a**. A blue shift is observable relative to the spectrum of its isomer **4a**. The band at approximately 311 nm for compound **4a** (figure 2), which can be attributed to the cinnamate moiety of compound **4a**, shifts to about 276 nm in the case of compound **6a** (see figure 3). This shift can be explained by the fact that the electron-donating alkoxy group, substituted at the *para*-position of the cinnamate group of compound **4a**, is replaced by a weaker electron-donating arylcarbonyloxy group in compound **6a**. The same holds for compounds **5a** and **7a**. These blue shifts explain why **6a** and **7a** isomerized

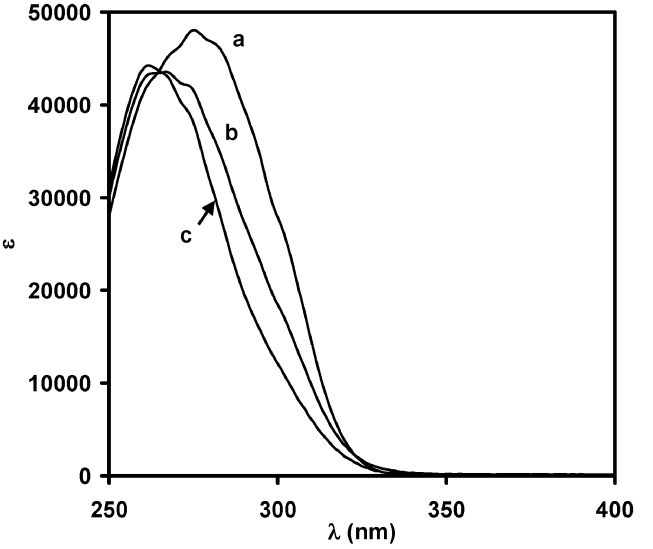

Figure 3. Absorption UV spectra of a solution of **6a** in acetonitrile (a) before and (b) after irradiation with the TL-08 lamp, and (c) of a solution of **7a** in acetonitrile.

only when the TL-08 lamp was used. Prolonged irradiation of **6a** and **7a** led to very small spectral changes in the UV spectra and some small new signals of unknown origins in the ^{1}H NMR spectra in dichloromethane. It is possible that the benzoyloxycinnamate group in compounds **6a** and **7a** is more susceptible to a photo-Fries rearrangement [26] than is the benzoyloxybenzoate group in compounds **4a** and **5a**. This may explain the formation of by-products in the case of **6a** and **7a**. Concerning application in cholesteric colour filters, these side-reactions will not cause problems since they were observed only long after the formation of the photostationary state.

By measuring the pitch of the helix in the photostationary state (p_{PSS}) after irradiation of the mixtures of **4a** or **6a** with E7, the *HTP* in the photostationary state (HTP_{PSS}) can be determined, and is defined as:

$$HTP_{PSS} = \frac{1}{p_{PSS}(x_E + x_Z)} \tag{2}$$

and the degree of conversion (c) to the *Z*-isomer **5a** or **7a**, respectively, can be calculated according to:

$$c = \frac{HTP_E - HTP_{PSS}}{HTP_E - HTP_Z} \times 100\%. \tag{3}$$

The degree of conversion of the *Z*-isomers to the *E*-isomers can of course be measured in the same way. The results of these measurements are presented in table 1. These data compare well with those obtained from the UV spectra. Only in the case of compounds **6a** and **7a** were some deviations found. Apart from the relatively

low accuracy of the *HTP* measurements, it is possible that the photostationary state in E7, the medium in which the *HTP* was measured, is different from that in acetonitrile, the medium in which the UV spectra were measured. Whatever the case, both the *HTP* and UV measurements show that the *E–Z* conversion of compounds **4a** and **6a** is sufficient to change the reflection colour in cholesteric colour filters over the entire visible region.

3.5. *Properties and photochemistry of compounds 4b and 6b*

The properties of diacrylates **4b** and **6b** are also presented in table 1. Comparison with their non-acrylate analogues **4a** and **6a**, respectively, shows that the acrylates have lower melting points and lower *HTP* values. Lowering of the melting point is frequently observed when acrylate groups are attached to liquid crystals [27]. It was for example also observed in the case of the menthone-derived materials **1a** and **1b**. The lower *HTP* values are partly attributable to the fact that these values are determined with the aid of the weight fraction, equation (1), and the molecular weights of the acrylate-derived materials **4b** and **6b** are approximately 20% higher than those of the non-acrylates **4a** and **6a**. A difference in interaction between these diacrylates and the non-polymerizable analogues with the host materials may also result in different *HTP* values. The UV spectra of the diacrylates **4b** and **6b** are identical to those of the non-acrylates **4a** and **6a**, respectively. The same spectral changes were observed upon irradiation. It is therefore assumed that the photochemical behaviour of the diacrylates is the same as that of the non-acrylates. Table 1 shows that the HTP_{PSS} (*HTP* in the photostationary state) of both compounds is more than a factor of 2 lower than HTP_E. This means that the pitch changes upon irradiation are sufficient to change the reflection colour in cholesteric layers from blue to red. These diacrylates can therefore be used in cholesteric colour filter manufacturing.

3.6. *Irradiated cholesteric layers*

Cholesteric layers were made by spin-coating a mixture of one of compounds **4b** or **6b** with the nematic diacrylates RM82 and RM257 and the photoinitiator in xylene onto a rubbed polyimide layer. The advantage of using these nematic diacrylates is that they crystallize very slowly, which means that the liquid film can be handled at room temperature (i.e. in the undercooled state). An addition of 8 wt % of the chiral diacrylates **4b** or **6b** was used in the mixtures to obtain layers which after spin-coating exhibited a reflection wavelength (λ_{max}) of approximately 430 nm. The *HTP* values of the compounds in this medium can be calculated with equation (1). An *HTP* value of about 46 μm^{-1} was determined using a mean refractive index of about 1.6 for these materials after polymerization [27]. This value is similar to that obtained in E7. The cholesteric layers reflected right-handed circularly polarized light, which is in accordance with the observation of the right-handed helix in E7 (see table 1). So the behaviour of compounds **4b** and **6b** in the RM257/RM82 mixture is similar to that in E7. Upon UV irradiation of the layers (in air to avoid polymerization) only minor colour changes were observed. The colour changes increased and stabilized after heating at 70°C for about 1 min. The lower viscosity of the layer at 70°C facilitates fast change of the cholesteric helix. This effect was also observed with the menthone derivative **1b** mixed with similar nematic diacrylates [4, 5].

Figure 4 shows the transmission spectra of cholesteric polymeric layers made with compound **6b**. Spectrum a was obtained without photoisomerization. The other spectra were obtained using the isomerization reaction. In order to ensure good conversion of the cinnamic derivative, a Philips HPA lamp system with sufficient intensity below 365 nm was used. The layers were then polymerized in a nitrogen atmosphere using the same lamp system, followed by 1.5 h thermal polymerization (post-bake) in nitrogen at 150°C. Identical spectra were obtained with layers formed with compound **4b**. To

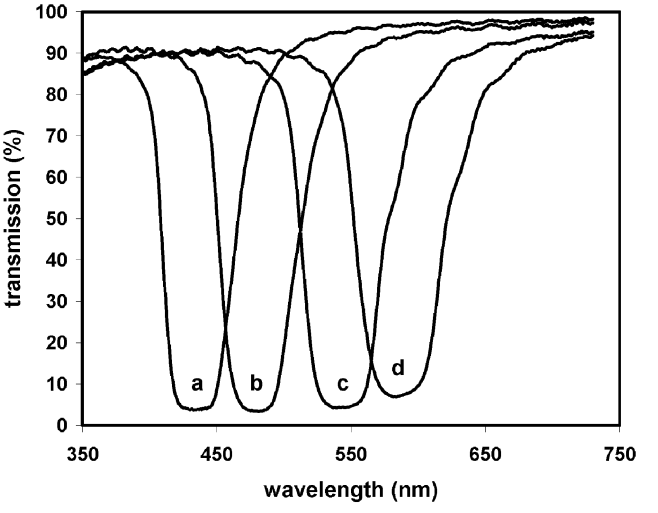

Figure 4. Transmission spectra (using right-handed circularly polarized light) of a 3.5 μm thick cholesteric polymeric film consisting of a copolymer of RM82, RM257 and 8% compound **6b** without photoisomerization before polymerization (a). Spectra b, c and d were obtained after photoisomerization before polymerization, with the irradiation times of the photoisomerization reaction increasing in the order b<c<d.

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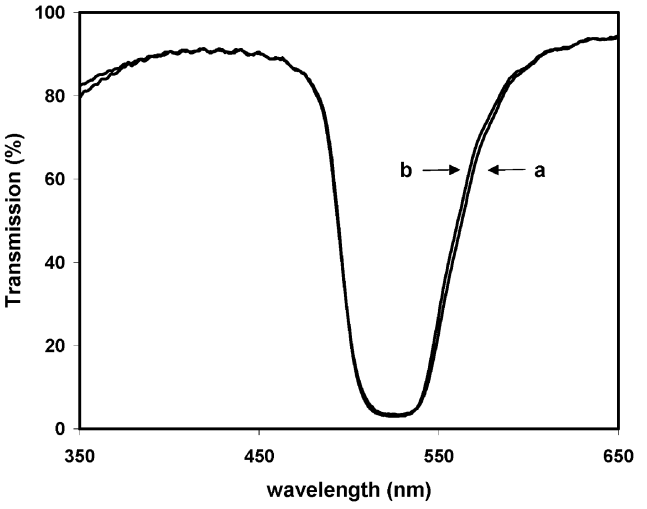

Figure 5. Transmission spectra (using right-handed circularly polarized light) of a 3.5 µm thick cholesteric polymeric film of a copolymer of RM82, RM257 and 8% isomerizable compound **6b** photoisomerized before polymerization until a reflection wavelength of about 525 nm was obtained (a) before and (b) after heating at 200°C for 6 h.

assess the thermal stability, a sample made from **6b**, irradiated until a reflection wavelength of 525 nm (measured after polymerization) was obtained, was heated at 200°C for 6 h. Figure 5 shows the spectra obtained after preparation and after the heating process. No significant change was observed. The same result was obtained with a polymer film prepared with **4b**. For comparison, a polymer film made in the same manner using menthone compound **1b** showed a blue shift of approximately 10 nm after heating at 200°C for 6 h [9]. So the films made with the new isosorbide-derived compounds have an enhanced thermal stability, which is of importance when these films are processed further in the manufacturing of reflective liquid crystal displays. There are several factors that probably contribute to this better stability. First, the isosorbide and cinnamate structures are more stable than the structure of the menthone derivative. Second, less chiral compound is needed. Third, the use of the new chiral diacrylates leads to more crosslinks than with the menthone derivative. The role of crosslinking could be investigated with monoacrylates derived from isosorbide. It should be rather easy to prepare especially monoacrylates with structures similar to those of **4a** and **4b** because the side groups are linked to the isosorbide moiety sequentially, as can be seen in scheme 1. It would also be possible to use nematic materials containing monoacrylates with structures similar to those of the nematic diacrylates used in this study. Future research will focus on this type of acrylates to find out why the cholesteric layers made with compounds **4b** and **6b** are more stable than those made with the menthone derivative **1b**. The most important result is that compounds **4b** and **6b** are very suitable for use in the manufacture of cholesteric colour filters.

4. Conclusions

Isosorbide- and cinnamate-derived photoisomerizable compounds **4a** and **6a** exhibit high *HTP* values. Their *Z*-isomers **5a** and **7a**, respectively, show opposite handedness of the helix with respect to the *E*-isomers. Photoisomerisation starting with the *E*- or *Z*-isomer results in the same photostationary state, which contains an excess of the *Z*-isomer. The pitch changes induced by the photoisomerization of the *E*-isomers are large enough to change the reflection colour in cholesteric layers from blue to red. To assess their suitability for use in the production of cholesteric colour filters, the diacrylate analogues of **4a** and **6a**, **4b** and **6b**, respectively, were prepared. Films produced by spin-coating mixtures of one of these diacrylic isosorbide derivatives with nematic diacrylates changed colour by the photoisomerization reaction and were subsequently stabilized by polymerization. Such cholesteric films are thermally very stable and the new compounds are therefore very suitable for use in the manufacture of cholesteric colour filters.

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