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Chiral 2,2-disubstituted oxirane ethers and carboxylic esters. New ferroelectric liquid crystals and dopants for induced ferroelectric phases

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Chiral 2,2-disubstituted oxirane ethers and carboxylic esters

New ferroelectric liquid crystals and dopants for induced ferroelectric phases

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The synthesis, phase behaviour and spontaneous polarization of a new class of chiral LCs and chiral dopants for induced ferroelectric phases of general structure A, possessing a (2*S*)-2-hydroxymethyloxirane unit, and B, possessing a (2*R*)-2-oxirane carboxylic acid unit connected to mesogenic building blocks are described. One of these new compounds exhibits a S_C^* phase. A carbonyl group adjacent to the oxirane ring does not increase the spontaneous polarization which is in contrast to the results obtained for 2,3-disubstituted oxiranes. A comparison with analogous species containing a (2*S*)-2-hydroxymethyloxetane, a (2*R*)-2-hydroxymethylthiirane or a (2*S*,3*R*)-2-hydroxymethyloxirane unit is given.

1. Introduction

Ferroelectricity in liquid crystals (FLCs), first reported and soon afterwards experimentally demonstrated by Meyer [1], now attracts great interest in both fundamental research and technological applications.

The great advantage of ferroelectric liquid crystals which makes them extremely interesting as materials for liquid crystal displays is their fast electrooptical response. Nematic liquid crystal (NLC) displays are well established, useful and today still by far the most applied, but they suffer from a specific disadvantage: their relatively slow switching process makes them unsuitable for applications requiring rapid cycling of the on/off states. Switching from the off to the on state can be carried out in approximately 1 microsecond. But, because of their fundamental mode of operation, the on to off state switching process of even the best developed NLC displays is slower than 1 millisecond. The reason for this behaviour is the necessarily involved molecular relaxation process, which defies any attempts at acceleration. In ferroelectric liquid crystals displays generally, use is made of the effect of surface stabilization [2] (SSFLC), resulting in unwinding of the helical superstructure of the S_C^* phase. These displays allow active switching in both directions between two stable states. Presently practical switching times of less than 5 microseconds are within reach, and in principle less than 1 microsecond will be possible.

Preceding investigations have shown favourable ferroelectric properties for chiral 2,3-disubstituted oxiranes as materials for FLC applications. Especially *cis*-2,3-disubstituted oxirane carboxylic esters exhibit the very high values of the spontaneous polarization which are required for fast switching. For a 10 per cent mixture of compound **1**, for example, a P_S value of 77 nC cm^{-2} has been measured [3]. These results inspired us to synthesize 2,2-disubstituted oxiranes of type A and type B.

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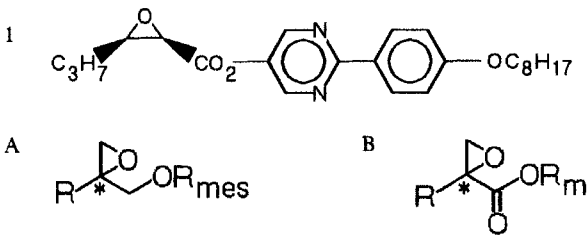
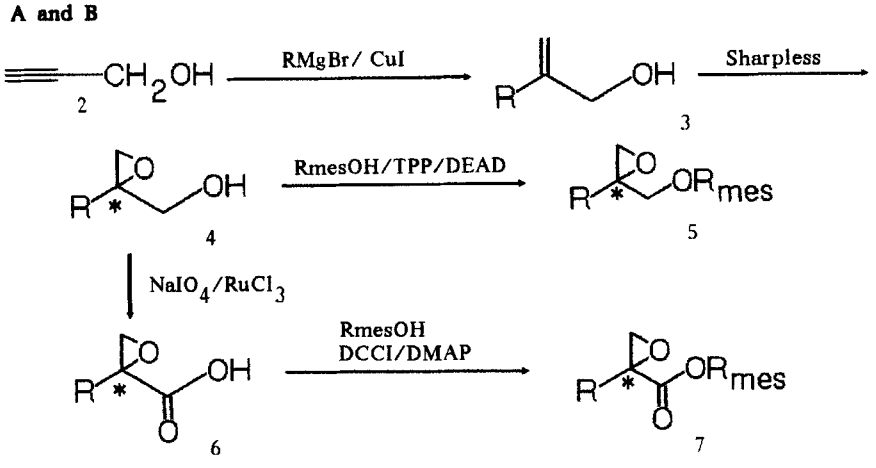


A structural comparison of the known 2,3-disubstituted with the new 2,2-disubstituted oxiranes leads to the following reflections: the moiety in the molecule containing the necessary dipole moment remains the same, but the substitution at the oxirane ring is changed. In A and B, there is only one centre of chirality and the chiral region is more flexible. Therefore a somewhat diminished P_S value is to be expected. On the other hand however, this effect could be completely or partially compensated or perhaps turned into the reverse due to the protruding oxirane ring, which causes a larger rotational hindrance. It has been observed that restriction of the rotation around the long axis of the molecule near the polar group has a favourable impact on the spontaneous polarization.

Furthermore, a comparison of the oxirane ethers A and the oxirane esters B was of interest. For 2,3-disubstituted 2-oxirane carboxylic esters, due to the enhancement of the oxirane dipole by the adjacent carbonyl group, we found generally higher P_S values compared with the analogous ethers [4]. Will this effect also be valid for A and B?

2. Synthesis

Liquid crystal materials containing the chiral 2,2-disubstituted oxirane unit were synthesized starting from propargyl alcohol **2** (see the scheme). Copper(I)iodide catalysed regiospecific addition of **2** with Grignard reagents afforded the 2-methylene alcohols **3** [5]. These allylic alcohols were transformed into the chiral 2,2-disubstituted epoxy alcohols **4** by the catalytic Sharpless reaction [6]. Etherification of the alcohols **4** with mesogenic phenols was accomplished by the Mitsunobu reaction [7] yielding the ethers **5** (see table 1). The 2,3-disubstituted oxirane ether **10** (see table 2) was synthesized for comparison in an analogous manner starting from *Z*-2-decen-1-ol. Oxidation of **4**



Scheme

to the corresponding oxirane carboxylic acid **6** was carried out using $RuCl_3$ (catalytic amounts)/$NaIO_4$, in a two phase system [8]. Steglich esterification of **6** with mesogenic phenols gave the carboxylic esters **7** [9] (see table 1).

The thiirane **9** (see table 2) was synthesized by reaction of **5b** with triphenylphosphinesulphide and trifluoroacetic acid [10]. The oxetane ether **8** (see table 2) was obtained by reaction of **5a** with trimethylsulphoxonium iodide and potassium *tert*-butoxide [11].

3. Spontaneous polarization

The induced spontaneous polarization was measured using 10 mol% solutions in the non-chiral host M89/85 (C 9°C S_C 84°C S_A 93°C N 105°C I) from Hoechst AG. The P_S values presented are those for the 10 mol% solutions and are not extrapolated. The helical twisting power (*HTP*) was determined for the cholesteric phase of the mixtures, using the Cano wedge method.

4. Phase behaviour

The compounds with only two aromatic rings in the mesogenic part of the molecule show no mesophases. For the oxirane ester **7a** two crystal modifications are observed. The oxirane ether **5b**, with three rings exhibits a cholesteric and a smectic C* phase. The S_C^* phase changes to a S_A phase when the oxygen in **5b** is exchanged for sulphur (see **9**), while the cholesteric phase is lost.

Table 1

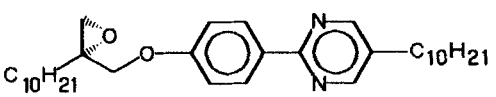
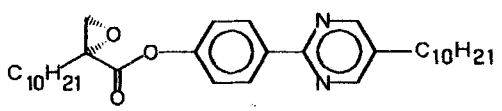
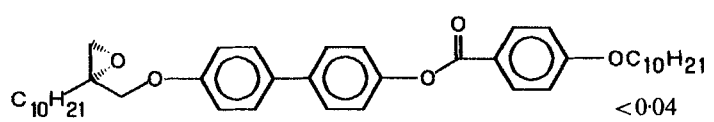
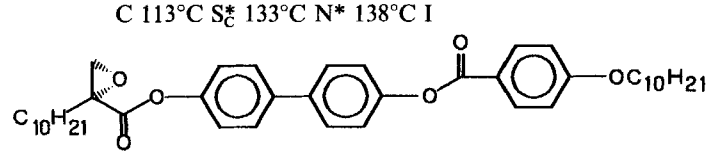
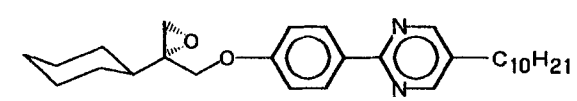
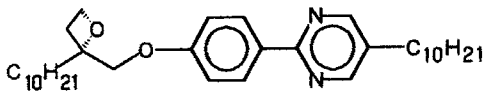
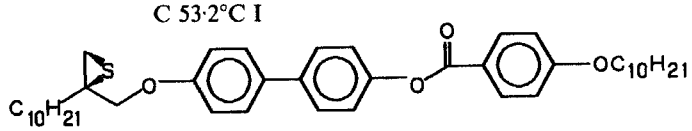
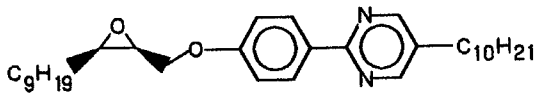
		HTP/μm^{-1}	P_S/nC cm^{-2}
5a		+0·24 (77°C)	−9·9 (25·0°C)
	C 57·3°C I		
7a		+5·14 (77°C)	−8·1 (23·4°C)
	C_1 63·0°C C_2 74·8°C I		
5b		<0·04	−4·0 (40·0°C) −145 in S_C^* (115°C)
	C 113°C S_C^* 133°C N* 138°C I		
7b			−1·9 (23·5°C)
5c			−5·1 (27·3°C)
	Liquid at room temperature		

Table 2

		$HTP/\mu m^{-1}$	$P_S/nC\,cm^{-2}$
8	 C 53·2°C I		+2·5 (30·0°C)
9	 C 77·0°C S_A 91·2°C I		+1·4 (28·1°C)
10	 C 85·5°C I		+14·3 (27·0°C)

5. Discussion

The oxirane ethers of type A show higher P_S values than the esters **B**. This is in contrast to the results obtained with 2,3-disubstituted oxiranes, where the higher spontaneous polarization is observed in the ester series due to the interaction of the oxirane and carbonyl dipole as mentioned above. This cooperative effect has been proved by IR measurements. The 2,3-disubstituted oxirane carboxylic esters exhibit two preferred conformations (*syn* and *anti*) with distinguishable IR carbonyl absorptions [12]. In the *syn*-arrangement the dipoles cooperate (increasing the P_S value), whereas they compensate partially in the *anti*-arrangement. The normally disfavoured *syn*-conformation is energetically favoured in this case by *gauche*-attractive forces between oxirane ring and carbonyl group. IR measurements of oxirane carboxylic esters as dopants in nematic or S_C hosts show a larger intensity for the absorption of the *syn*-conformer (1760 cm^{-1}) than for the *anti*-conformer (1740 cm^{-1}). The increased overall lateral dipole moment causes a larger spontaneous polarization compared with the oxirane ethers.

We presume that in the case of the 2,2-disubstituted oxirane carboxylic esters the *syn*-conformation cannot be formed because of steric hindrance. This assumption coincides with considerations of space-filling models and IR measurements for **7a** showing only one carbonyl absorption in solution in $CHCl_3$ (1760 cm^{-1}), as well as in a nematic (1751 cm^{-1}) or smectic C host (1750 cm^{-1}).

The spontaneous polarization of the 2,2-disubstituted ethers (see **5a**) is not as high as for the analogous 2,3-*cis*-disubstituted ethers (see **10**), but is higher than for the 2,3-*trans*-disubstituted compounds. Changing the decyl chain in **5a** to a cyclohexyl-substituent (see **5c**) leads to a decrease in the spontaneous polarization from 9·9 to 5·1 $nC\,cm^{-2}$.

Enlargement of the spiro-connected oxirane ring in **5a** to give the four-membered oxetane ring **8** increases the rotational hindrance, but decreases the lateral dipole moment acting in the system. As a result of both competing effects on the polarization, we observe a distinct decrease in the P_S value. The oxetane ether **8** exhibits only 25 per cent of the induced P_S value of the analogous oxirane **5b**.

The enantioselective exchange of oxygen in the three-membered ring of **5b** by sulphur also leads to a distinct drop in the spontaneous polarization (see **9**). Only compound **5b** exhibits a S_C^* phase. It shows a high value of the spontaneous polarization ($P_S = -145\,nC\,cm^{-2}$).

6. Experimental

^1H NMR: Bruker WM 400. Specific optical rotation: Perkin–Elmer PE 141 polarimeter. Texture observations: JENAPOL polarizing microscope and Linkam THMSE 600 heating/freezing state. Measurements of spontaneous polarization: in test cells with a spacing between 2 and 3 μm. The glass substrates of the cells were coated with polyimide and both substrates were rubbed. The cells were filled by capillary interaction and were thermostatted during the measurements by a Linkam TMS 90 precision temperature control system. Spontaneous polarization was obtained by the triangular wave method [13]; applied voltage: *c.* 20 V, frequency: 80 Hz. The sign of the spontaneous polarization was determined by investigation of the switching behaviour, while considering the temperature dependence of the switching angle. Chromatographic purifications were performed using flash chromatography (FC) on ICN Biomedicals silica (32–63 μm). For reactions requiring anhydrous conditions, the glassware was flame-dried.

6.1. *Synthetic procedures for representative compounds*

6.1.1. *2-Methylene-1-dodecanol* **3**

Propargyl alcohol (1·401 g, 25·0 mmol) and copper(I)iodide (492 mg, 2·6 mmol) in 25 ml of anhydrous THF were treated at −20° with a diluted solution of a Grignard reagent in 46 ml of anhydrous THF prepared from magnesium (1·464 g, 6·02 mmol) and 1-bromodecane (13·59 g, 61·4 mmol) in 26 ml of dry THF. After 20 h of stirring and warming to room temperature, 60 ml of aqueous saturated ammonium chloride and 30 ml methyl *tert*-butyl ether (MTBE) were added and the mixture was strirred vigorously for 30 min. The phases were separated, the aqueous phase was shaken with MTBE and the combined organic phases were dried over magnesium sulphate. The crude product, obtained after removal of the solvent, was purified by FC, yielding 4·18 g (84 per cent) of 2-methylene-1-dodecanol as a colourless oil. ^1H NMR ($CDCl_3$): δV 0·88 (t, $J = 7$ Hz, 3 H), 1·20–1·34 (m, 17 H), 1·44 (quint, $J = 7$ Hz, 2 H), 2·05 (t(br), $J = 7$ Hz, 2 H), 4·06 (s(br) 2 H), 4·86 (m, 1 H), 5·00 p.p.m. (m, 1 H). MS (100°C): *m/e* 198 (1 per cent, M^+), 180 (1, $M-H_2O$), 166 (1, $M-H_2O-CH_2$), 152 (1), 138 (2), 124 (4), 110 (8), 96 (22), 82 (40), 71 (66), 57 (100).

6.1.2. *(2S)-2-Decyl-2-hydroxymethyloxirane* **4**

A mixture of powdered, commercially activated 4 Å molecular sieves (1·5 g) and 40 ml of anhydrous dichloromethane under nitrogen was cooled to 0°C. L-(+)-diethyl tartrate (L-(+)-DET; 385 mg, 2·61 mmol, 13·5 mol%) and titanium tetra-isopropoxide (555 mg, 1·95 mmol, 10 mol%) were added sequentially. After cooling the mixture to −25°C, a *tert*-butyl hydroperoxide solution (17 ml, 51 mmol; 3·0 M in toluene) was added within 20 min and the resulting mixture was stirred for 30 min, whereupon a solution of 2-methylene-1-dodecanol **3** (3·85 g, 19·4 mmol) in 8 ml of dry dichloromethane (dried over powdered 4 Å molecular sieves for 1 h prior to addition to the reaction solution) was added. Stirring was maintained for 35 min at *c.* −25°C. Thereafter the reaction mixture was refrigerated at −31°C for 13·5 h. After warming to 0°C, the catalyst was quenched by adding 10 ml of water and stirring for 1·25 h, while allowing

the reaction solution to warm to room temperature. Hydrolysis of the tartrate was affected by adding 2·6 ml of a 30 per cent aqueous solution of sodium hydroxide saturated with sodium chloride and stirring for 50 min. After phase separation, extraction of the aqueous phase with dichloromethane, drying over magnesium sulphate, removal of the solvent and FC 2·32 g (56 per cent) of (2*S*)-2-decyl-2-hydroxymethyloxirane were obtained as a colourless oil. $[\alpha]_D^{22} = -12{\cdot}1°$ (*c*. 12·0 mg in $CHCl_3$). ^1H NMR ($CDCl_3$): δ, 0·88 (t, $J = 7$ Hz, 3 H), 1·21–1·40 (m, 19 H), 1·46–1·54 (m, 1 H), 1·69 (dd, $J = 8{\cdot}5$ and 4 Hz, 1 H), 1·72–1·82 (m, 1 H), 2·66, 2·88 (AB, $J = 4{\cdot}5$ Hz, 2 H), 3·64 (dd, $J = 12$ and 8·5 Hz, 1 H), 3·77 p.p.m. (dd, $J = 12$ and 4 Hz, 1 H). MS (100°C): *m/e* 183 (4 per cent, M–CH_2OH), 165 (2, M–CH_2OH–H_2O), 124 (10), 111 (20), 97 (48), 95 (48), 88 (35), 83 (52), 74 (92), 71 (86), 69 (75), 57 (100), 55 (100).

6.1.3. (2*S*)-2-[4-(5-*Decylpyrimidin-2-yl*)*phenyloxymethyl*]-2-*decyloxirane* **5a**

A solution of (2*S*)-2-decyl-2-hydroxymethyloxirane **4** (214 mg, 1·00 mmol), 2-(4-hydroxyphenyl)-5-decylpyrimidine (312 mg, 1·00 mmol) and triphenylphosphine (262 mg, 1·00 mmol) under nitrogen was cooled to 0°C. Diethyl-azodicarboxylate (174 mg, 1·00 mmol) was added and the reaction mixture was stirred for 0·5 h at 0°C and for 3 days at room temperature. Concentration of the reaction mixture yielded a crude product which was purified by FC. The yield of (2*S*)-2-[4-(5-decylpyrimidin-2-yl)-phenyl-1-yloxymethyl]-2-decyloxirane **5a** was 400 mg (79 per cent). $[\alpha]_D^{24} = +2{\cdot}1°$ (*c* 5·0 mg in $CHCl_3$). ^1H NMR ($CDCl_3$: δ, 0·87 (t(br), $J = 7$ Hz, 6 H), 1·20–1·50 (m, 30 H), 1·64 (quint, $J = 7$ Hz, 2 H), 1·68 (ddd, $J = 14$, 9 and 7 Hz, 1 H), 1·90 (ddd, $J = 14$, 9·5 and 6 Hz, 1 H), 2·60 (t, $J = 7$ Hz, 2 H), 2·77, 2·87 (AB, $J = 4{\cdot}5$ Hz, 2 H), 4·05, 4·12 (AB, $J = 10{\cdot}5$ Hz, 2 H), 7·00, 8·35 (AA'BB', $J = 9$ Hz, 4 H), 8·57 p.p.m. (s, 2 H). MS (165°C): *m/e* 508 (3 per cent, M^+), 402 (13), 340 (20), 311 (61, RmesO), 91 (100).

6.1.4. (2*R*(-2-*Decyloxirane-2-carboxylic acid* **6**

2·5 ml of carbon tetrachloride, 2·5 ml of acetonitrile, 3·9 ml of water, (2*S*)-2-decyl-2-hydroxymethyloxirane (300 mg, 1·40 mmol), sodium metaperiodate (952 mg, 4·45 mmol; 3·2 equiv.) and ruthenium trichloride hydrate (18 mg, 0·087 mmol; 6·2 mol%) were stirred for 16 h. Then the reaction mixture was treated with 10 ml of aqueous saturated sodium chloride and 20 ml of dichloromethane and filtered. The phases were separated and the aqueous phase was shaken with dichloromethane. The combined organic phases were washed with saturated aqueous sodium chloride, dried over magnesium sulphate and concentrated. The (2*R*)-2-decyloxirane-2-carboxylic acid (290 mg, 91 per cent) was used for the next step without further purification. ^1H NMR ($CDCl_3$): δ, 0·88 (t, $J = 7$ Hz, 3 H), 1·17–1·37 (m, 18 H), 2·79, 3·01 p.p.m. (AB, $J = 6$ Hz, 2 H). MS (80°C): *m/e* 228 (6 per cent, M^+), 211 (27, M–OH), 169 (95), 105 (100).

6.1.5. (2*R*)-2-[4-(5-*Decylpyrimidin-2-yl*)*phenyl*] 2-*decyloxirane-2-carboxylate* **7a**

A solution of (2*R*)-2-decyloxirane-2-carboxylic acid **5** (359 mg, 1·57 mmol), *N,N*-dicyclohexylcarbodiimide (493 mg, 2·39 mmol), 2-(4-hydroxyphenyl)-5-decylpyrimidine (483 mg, 1·55 mmol) and 4,4-dimethylaminopyridine (26 mg, 0·21 mmol; 13 mol%) in 40 ml of dry dichloromethane was stirred at room temperature under nitrogen for 5 days. Precipitated *N,N*,-dicyclohexylurea was filted off and the filtrate was washed with saturated aqueous sodium chloride, dried over magnesium

sulphate and the solvent removed. The crude product was purified by FC, yielding 219 mg (27 per cent) of (2*R*)-2-[4-(5-decylpyrimidin-2-yl)-phenyl] 2-decyloxirane-2-carboxylate **7a** $[\alpha]_D^{24} = +2{\cdot}9°$ (*c* 4·2 mg in $CHCl_3$). ^1H NMR ($CDCl_3$): δ, 0·88 (t, $J = 7$ Hz, 6 H), 1·20–1·42 (m, 30 H), (quint, $J = 7$ Hz, 2 H), 1·80 (ddd, $J = 14$, 10 and 5·5 Hz, 1 H), 2·20 (ddd, $J = 14$, 10 and 5·5 Hz, 1 H), 2·62 (t, $J = 7$ Hz, 2 H), 2·93, 3·25 (AB, $J = 6$ Hz, 2 H), 7·21, 8·45 (AA'BB', $J = 9$ Hz, 4 H), 8·61 p.p.m. (s, 2 H). MS (90°C): *m/e* 522 (16 per cent, M^+), 506 (6, M–O), 494 (23), 381 (9, M–$C_{10}H_{21}$), 325 (68, RmesOCH_2), 312 (44, RmesOH), 297 (33), 199 (30), 185 (64), 69 (100).

6.1.6. (2*S*)-2-[4-(5-*Decylpyrimidin-2-yl*)*phenyloxymethyl*]-2-*decyloxetane* (**8**)

A mixture of trimethylsulphoxonium iodide (241 mg, 1·07 mmol) and potassium *tert*-butoxide (125 mg, 1·06 mmol) in 2 ml of dry *tert*-butanol under nitrogen was stirred for 30 min at 50°C. Thereafter (2*S*)-2-[4-(5-decylpyrimidin-2-yl)phenyloxymethyl]-2-decyloxirane **5a** (205 mg, 0·40 mmol) dissolved in a mixture of 6 ml of dry *tert*-butanol and 4 ml of dry THF (to improve the solubility of the compound) was added. The reaction was stirred for 8 h at 70°C. After cooling to room temperature, 9 ml of water and 27 ml of MTBE were added, followed by stirring for 10 min. The phases were separated, the aqueous phase was shaken twice with dichloromethane, the combined organic phases were dried over magnesium sulphate and the solvent was removed. The resulting crude product was purified by FC, yielding 133 mg (63 per cent of (2*S*)-2-[4-(5-decylpyrimidin-2-yl)phenyloxymethyl]-2-decyloxetane **8**. $[\alpha]_D^{23} = -5{\cdot}9°$ (*c*. 8·4 mg in $CHCl_3$). ^1H NMR ($CDCl_3$): δ, 0·88 (t, $J = 7$ Hz, 6 H), 1·21–1·40 (m, 28 H), 1·45 (quint., $J = 7$ Hz, 2 H), 1·64 (quint., $J = 7$ Hz, 2 H), 1·82 (m, 2 H), 2·52 (ddd, $J = 11$, 9 and 7 Hz, 1 H), 2·60 (t, $J = 7$ Hz, 2 H), 2·70 (ddd, $J = 11$, 9 and 6 Hz, 1 H), 4·03, 4·08 (AB, $J = 10$ Hz, 2 H), 4·50 (dt, $J = 9$ and 6 Hz, 1 H), 4·62 (ddd, $J = 9$, 7 and 6 Hz, 1 H), 7·05, 8·36 (AA'BB', $J = 9$ Hz, 4 H), 8·58 p.p.m. (s, 2 H). MS (90°C): *m/e* 522 (2 per cent, M^+), 492 (10, M–CH_2O), 351 (6), 326 (5), 312 (19, RmesOH), 227 (9), 199 (50, RmesOH–C_8H_{17}), 197 (73), 185 (20), 149 (46), 109 (33), 95 (46), 83 (65), 71 (73), 69 (67), 57 (100).

6.1.7. (2*R*)-2-[4-(4-*Decyloxybenzoyloxy*)*biphenyl-4'-yl*]-*oxymethyl-2-decylthiirane* (**9**)

(2*S*)-2-[4-(4-Decyloxybenzoyloxy)biphenyl-4-yl]-oxymethyl-2-decyloxirane **5b** (145 mg, 0·226 mmol) and triphenylphosphinesulphide (76 mg, 0·26 mmol) were dissolved in 3 ml of dry toluene under nitrogen and trifluoroacetic acid (32 mg, 0·28 mmol) dissolved in 0·6 ml of dry toluene was added. The reaction solution was stirred for 5 days at room temperature, followed by treatment with sodium carbonate (38 mg, 0·36 mmol) and stirring for 45 min. The reaction mixture was diluted with 50 ml of MTBE, washed with 20 ml of saturated aqueous sodium chloride and dried over magnesium sulphate. Removal of the solvent and purification by FC yielded 67 mg (43 per cent) of (2*R*)-2-[4-(4-decyloxybenzoyloxy)-biphenyl-4-yl]-oxymethyl-2-decylthiirane **9**. $[\alpha]_D^{29} = -5{\cdot}6°$ (*c* 6·5 mg in $CHCl_3$). ^1H NMR ($CDCl_3$): δ, 0·87 (t, $J = 7$ Hz, 3 H), 0·89 (t, $J = 7$ Hz, 3 H), 1·20–1·66 (m, 33 H), 1·83 (quint, $J = 7$ Hz, 2 H), 2·28 (m, 1 H), 2·49 (s(br), 1 H), 2·53 (s(br), 1 H), 4·05 (t, $J = 7$ Hz, 2 H), 3·86, 4·31 (AB, $J = 10$ Hz, 2 H), 6·97, 6·98 (AB, $J = 9$ Hz, 2 H), 7·25, 7·58 (AA'BB', $J = 9$ Hz, 4 H), 7·52, 8·16 p.p.m. (AA'BB', $J = 9$ Hz, 4 H. MS (270°C): *m/e* 626 (7 per cent, M–S), 261 (100) 192 (25), 160 (23), 121 (36), 64 (53).

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