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Novel ferroelectric liquid crystals and dopants for induced ferroelectric phases containing 3,4-epoxy-2-octanols as chiral unit

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The synthesis of a new class of chiral smectic liquid crystals is described, along with transition temperatures, phase behaviour, spontaneous polarizations and related data. The general structure is shown in A, possessing a chiral unit derived from 3,4-epoxy-2-octanol. Two of these new compounds show seemingly antiferroelectric behaviour. The influence of the mesogenic core structure on mesophase behaviour and ferroelectric properties was investigated. The non-liquid crystalline representatives were examined as dopants for induced ferroelectric phases in an achiral matrix.

1. Introduction

Since the discovery of ferroelectricity in liquid crystals by Meyer *et al.* in 1975 [1], our basic knowledge on structure/property relations has increased considerably and substance parameters with respect to display applications have been improved substantially. In comparison with today's commonly used TN ('twisted nematic') cells, FLC (ferroelectric liquid crystal) displays have the advantages of very short switching times, high contrast and wide viewing angle [2]. In TN-LC displays, the switching involves relaxation processes, whereas FLC devices are switchable between two stable states. For applications, ferroelectric materials with a broad S_C^* phase range, medium to high spontaneous polarization and low rotational viscosity are favourable.

In 1987 antiferroelectricity in chiral smectic liquid crystals was observed for the first time, when investigating 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxy-biphenyl-4-carboxylate (MHPOBC). The appearance of a third switching state, in addition to the known bistable ferroelectric states, is characteristic for the antiferroelectric phase, designated as S_{CA}^* [3–5]. Structural investigations proved that the tilt direction of the molecules alternates in successive layers (herringbone structure). Thus the direction of the spontaneous polarization is opposite in adjacent layers, hence cancelling out in the bulk sample. An electric field induces a transition from the antiferroelectric S_{CA}^* to the ferroelectric S_C^* state. The suitability of antiferroelectric liquid crystals for display devices was proven successfully recently [6]. First prototypes of antiferroelectric flat-panel displays have been demonstrated [7].

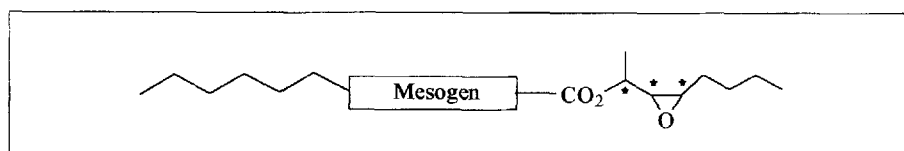
The oxirane unit was found to be a useful chiral moiety for ferroelectric liquid crystals [8, 9]. These thermostable materials have been claimed in several patents for application in device technology [10(a)]. One of these FLC epoxy compounds exhibits the hitherto highest published value of spontaneous polarization ($P_S = 1300 \text{ nC cm}^{-2}$) [10(b)]. During the evolution of the Boulder Model, Walba *et al.* used a *trans*-substituted 1-methyl-2,3-epoxyalkoxy system [11]. This system showed a relatively high spontaneous polarization ($P_S = 116 \text{ nC cm}^{-2}$). As previously investigated, a large difference in the P_S values between *trans*- and *cis*-configured oxiranes [12] exists. Because of rotational hindrance of the laterally acting dipole moment of the *cis*-oxiranes a high spontaneous polarization evolves.

These features inspired us to synthesize *cis*-3,4-epoxy-2-octyl esters of mesogenic carboxylic acids as shown in structure A. The new chiral building block contains three chiral centres and combines the known favourable properties of the chiral 2-octyl unit and the *cis*-oxirane moiety. For comparison the same mesogenic acids were combined with the unbranched *cis*- and *trans*-2,3-epoxyoctanols to observe the influence of the additional third chiral centre.

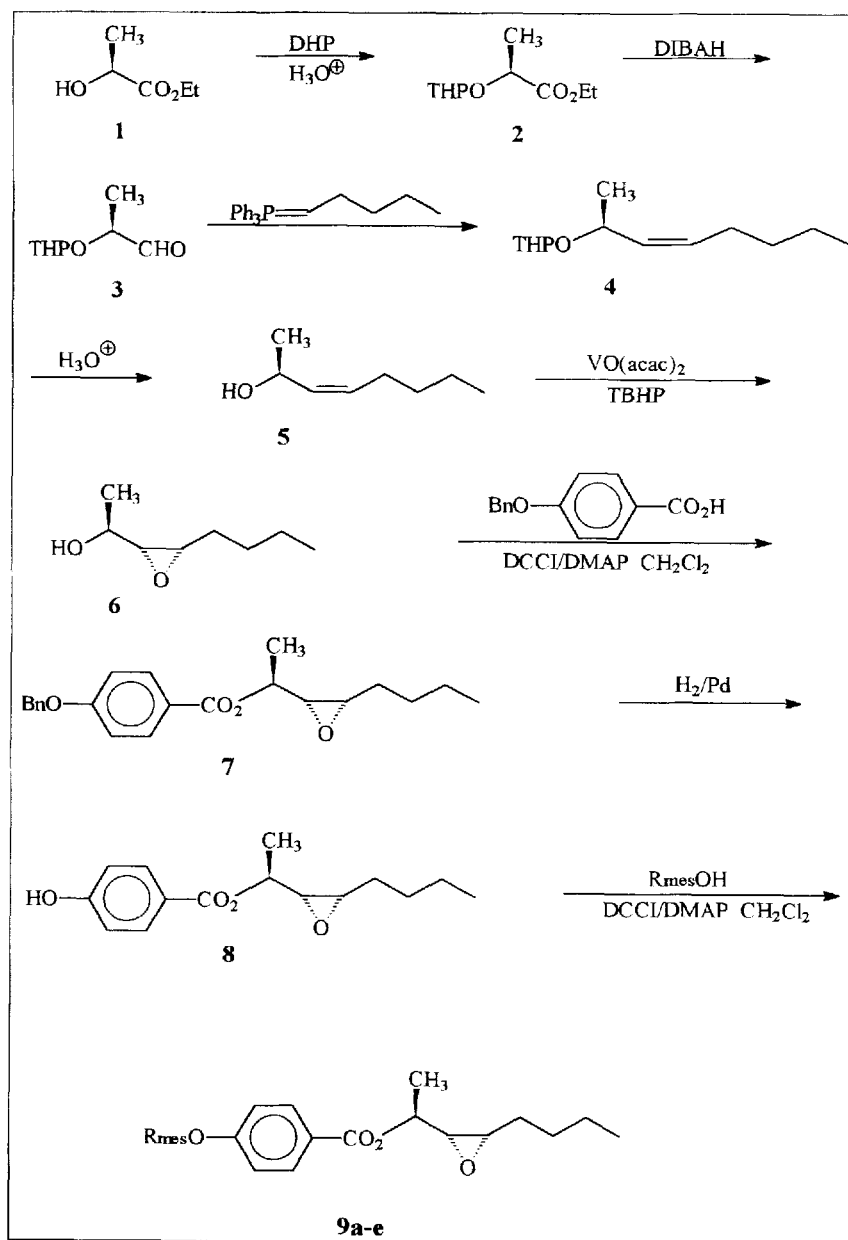
2. Synthesis

Optically active 3,4-epoxy-2-octanols were prepared as shown in scheme 1. (*S*)-(-)-Ethyl lactate **1** was used as starting material. After protection of the hydroxy group [13], the lactic ester group was transformed to the aldehyde **3** [14] using DIBAH [15] under mild conditions. The *cis*-configured allylic alcohol **5** [16] was obtained via the Wittig reaction [17] and subsequent deprotection. The chirogenic step was the diastereo-

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A General structure of substituted oxirane derivatives.



Scheme 1 Synthetic pathway to the compounds 9 a-e.

selective oxidation of **5** with *t*-butyl hydroperoxide in the presence of vanadyl acetylacetonate and gave the threo (anti) epoxide **6** [18] almost exclusively. The *syn* by-product could be separated by chromatography. The

directing effect of the hydroxy function at the chiral centre controls the asymmetric epoxidation. The formation of an intermediate in which the allylic hydroxy group is coordinated to the metal is suggested. The

epoxidation of the double bond takes place in a vanadate ester in a conformation which minimises steric interactions among the various substituents. Esterification of the epoxy alcohol with 4-benzyloxybenzoic acid using dicyclohexylcarbodiimide and 4-*N,N*-dimethylaminopyridine [19] led to the carboxylic ester **7**, which after deprotection was esterified with different mesogenic carboxylic acids to yield the target molecules **9a–e** (figure 1).

The unbranched chiral systems were synthesized via the Wittig reaction on pentanal **10** using triethyl phos-

phonoacetate **11** to give the α,β -unsaturated ester **12** [20] (scheme 2). The ester group was reduced by DIBAH to the *trans*-configured allylic alcohol **13** [21]. Epoxidation of **13** under Sharpless conditions [22] led to the epoxide **14** [23], which was esterified with 4-benzyloxybenzoic acid. After deprotection of the hydroxy function, the mesogenic carboxylic acid was esterified, to obtain **17**.

The synthetic route to the *cis*-configured 2,3-epoxyoctanol **23** (scheme 3) started with the protection of propargyl alcohol **18** [24], followed by alkylation

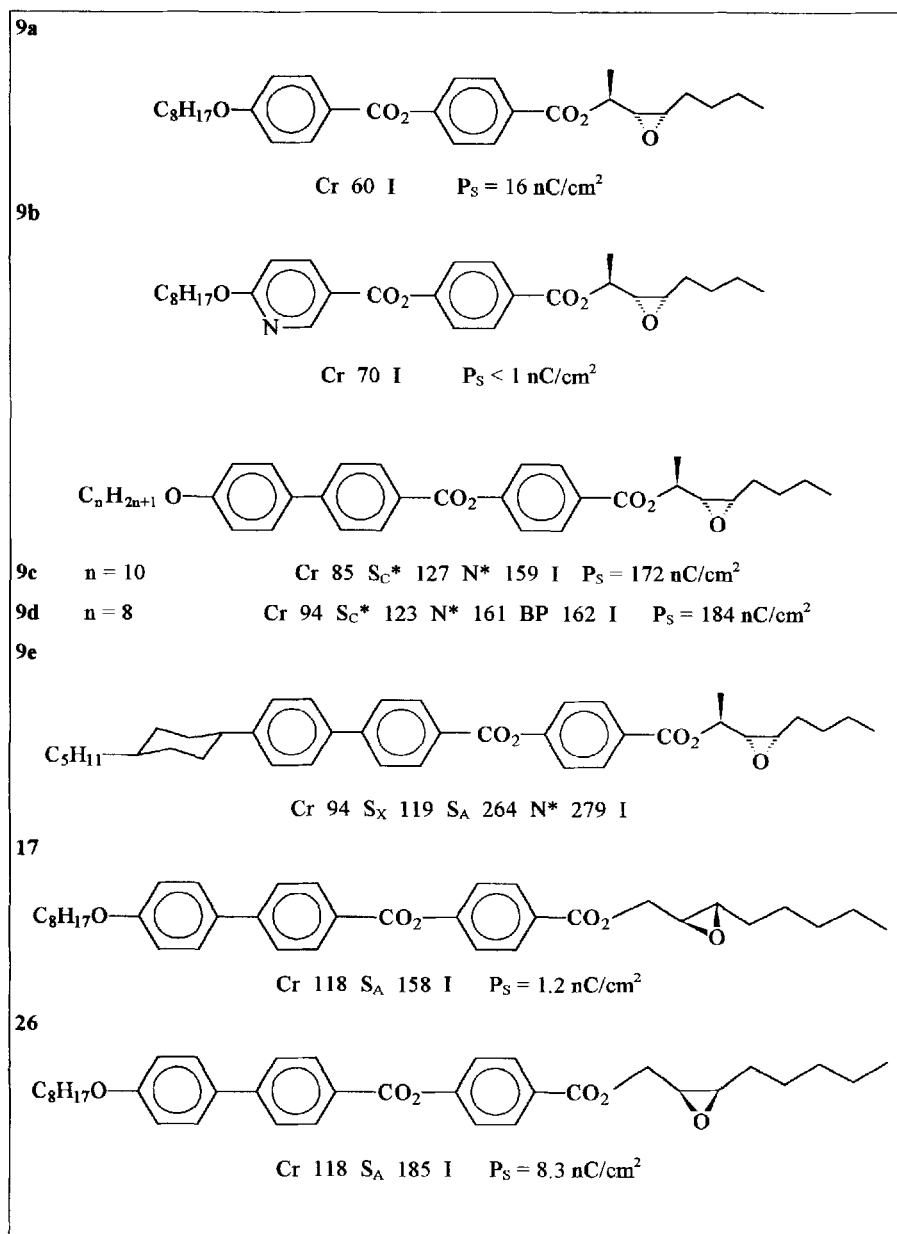
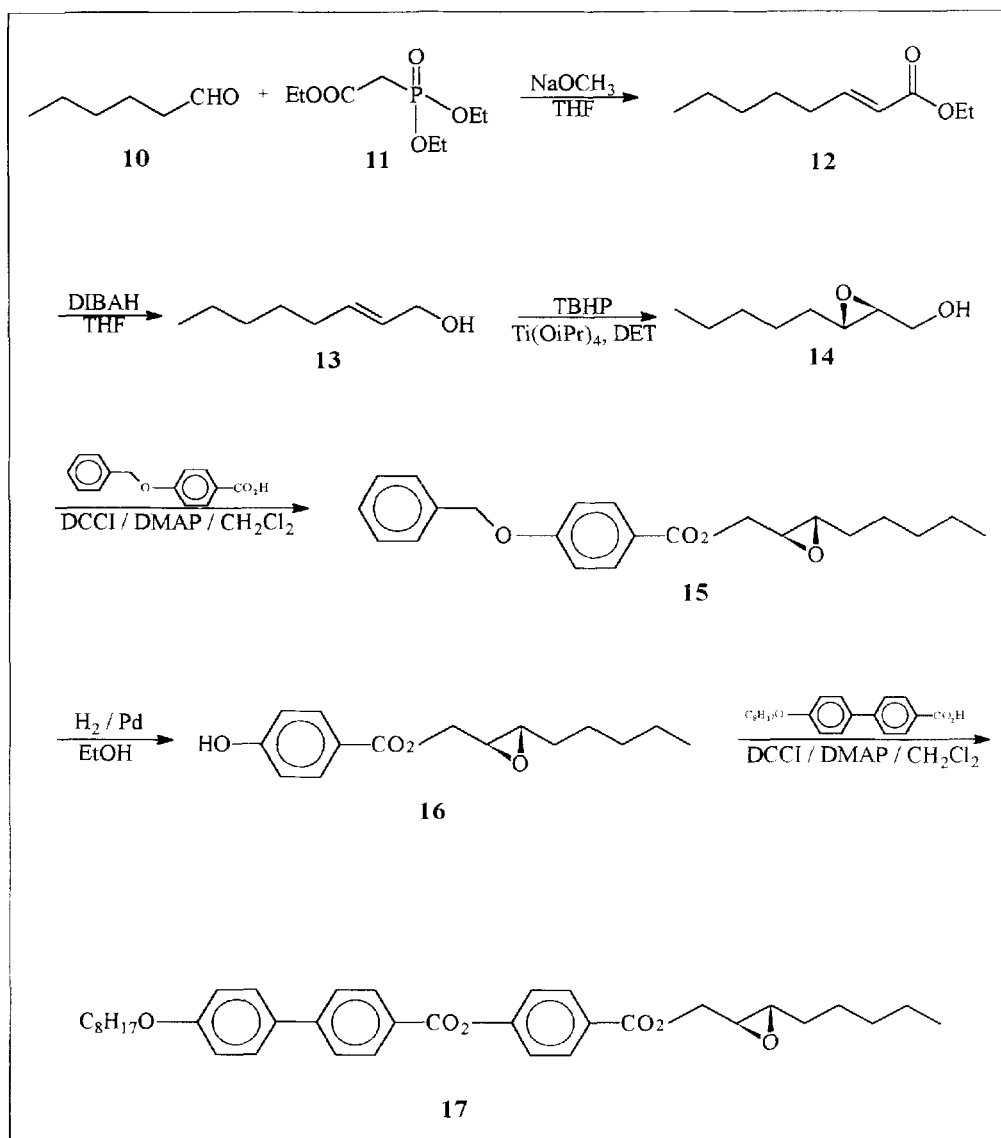


Figure 1. Synthesized compounds with related data; transition temperatures in $^{\circ}\text{C}$.



Scheme 2 Synthetic route to compound 17.

with iodopentane in the presence of BuLi [25]. Hydrogenolysis according to Lindlar conditions led to the *cis*-configured alkene 21 [26]. After deprotection, the allylic alcohol 22 was oxidized with *t*-butyl hydroperoxide in the presence of tetra-isopropyl orthotitanate and *L*-(+)-diethyl tartrate to give epoxide 23 [27]. Esterification with 4-benzyloxybenzoic acid followed by hydrogenolysis of the benzyl ether led to the phenol 25, which was esterified with the mesogenic carboxylic acid to yield 26.

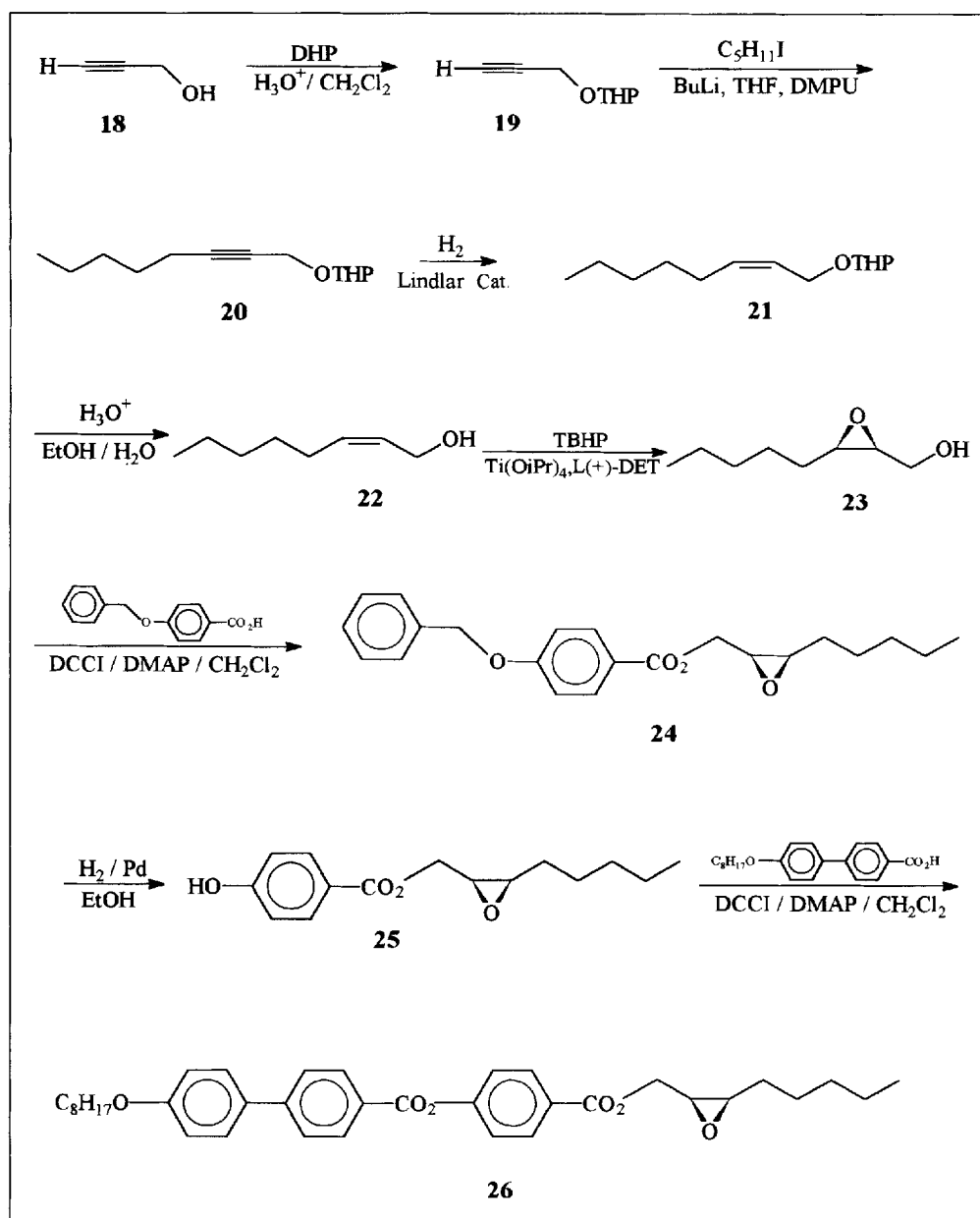
3. Spontaneous polarization

The induced spontaneous polarization was measured by the triangular wave method [28] using 10 mol %

solutions of 9a, b, e in the non-chiral host M89/85 (Cr 9°C S_C 84°C S_A 98°C N 105°C I) from Hoechst AG. The values of spontaneous polarization are not extrapolated.

4. Results and discussion

The compounds with two aromatic rings in the mesogenic part of the rod-like molecules (9a, 9b) exhibit no mesophases. Therefore their suitability as chiral dopants was tested. Both compounds induce an S_C* phase in the host. The spontaneous polarization of compound 9a in the mixture (Cr 9°C S_C* 94°C S_A 99°C N* 114°C I) has a maximum of 16 nC cm⁻² at 36°C, whereas compound

Scheme 3 Synthetic route to compound **26**.

9b (mixture: Cr 9°C S_C^* 85°C N* 93°C I) induces a P_S value below 1 nC cm^{-2} .

Variation of the mesogenic moiety to those containing three aromatic rings in the esters led to **9c** and **9d**. The substance **9c** exhibits two mesophases: a chiral smectic and a cholesteric phase. **9d** shows the same phase sequence, but additionally forms a blue phase in the UV-region. The temperature dependence of the spontaneous polarization observed for **9c** and **9d** is shown in figures 2 and 3. The S_C^* phases show seemingly antiferroelectric behaviour with typical tristate switching at low

frequencies (0.1 and 1 Hz). The S_C^* phases can be supercooled about 15–20 K. The switching is characterized by a d.c. threshold of 9 V for **9c**. The switching time at 125°C is $30 \mu\text{s}$ and the corresponding switching angle is 29° . At low frequencies, the T (transmittance)- E curve reveals a double hysteresis loop (figure 4) which is characteristic of an antiferroelectric behaviour, due to a tristate switching between the two ferroelectric states and the antiferroelectric state. P_S -measurements under an applied triangular voltage exhibit two current response peaks.

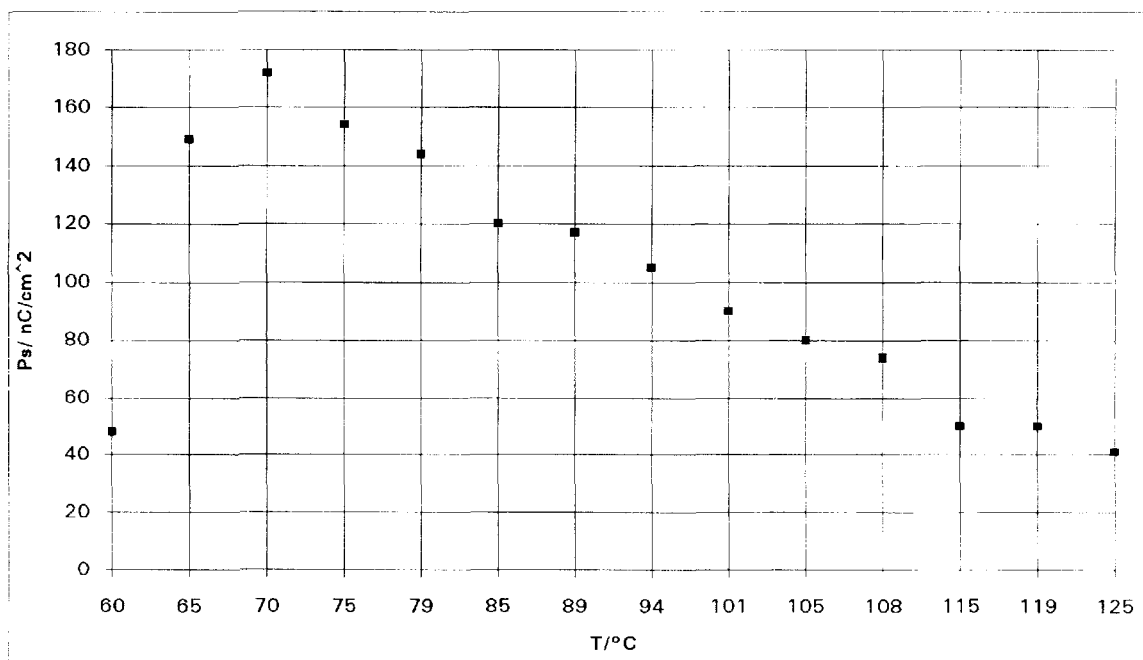


Figure 2. Temperature dependence of the spontaneous polarization of **9c**.

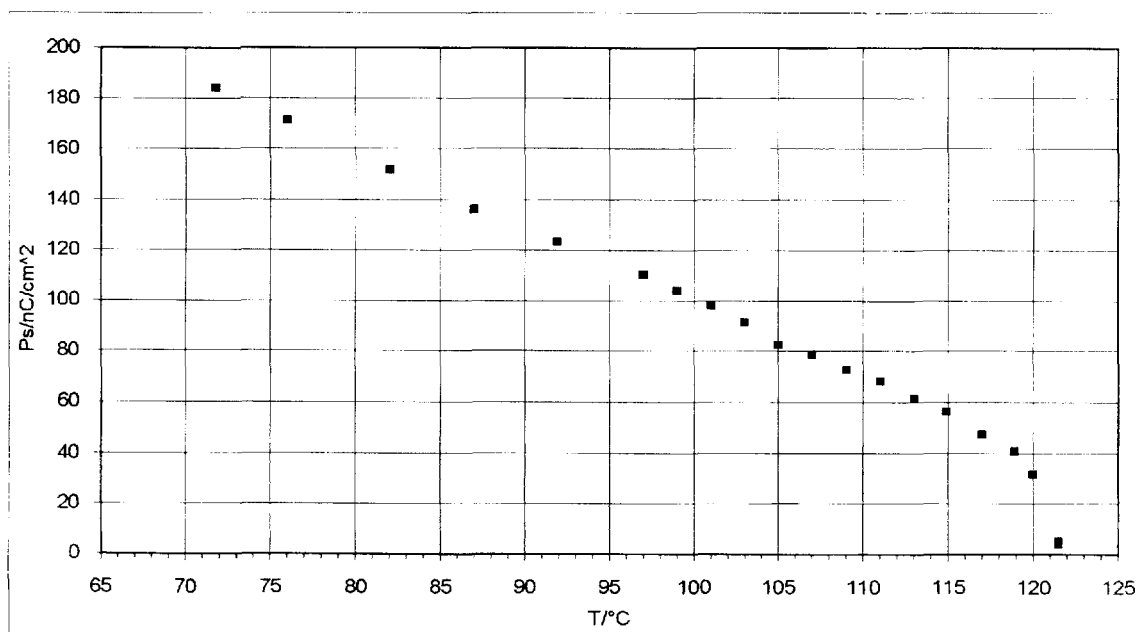


Figure 3. Temperature dependence of the spontaneous polarization of **9d**.

To designate the apparent antiferroelectric phase, miscibility studies with the antiferroelectric phase of MHPOBC were made. The mixture possesses a sharp phase boundary, which means that the assumption of the existence of an antiferroelectric phase seems to be incorrect. Dielectric studies confirm that as well. It appears to be a smectic C* phase with anomalous

electric switching behaviour. This phenomenon has been observed with other liquid crystalline materials possessing an S_C*-N* phase sequence [29]. The S_C* phase forms a stripe-like quasi-periodic texture, consisting of two types of domain with different directions of the smectic layer normal. Phases with such a stripe texture exhibit a behaviour similar to that of an antiferroelectric

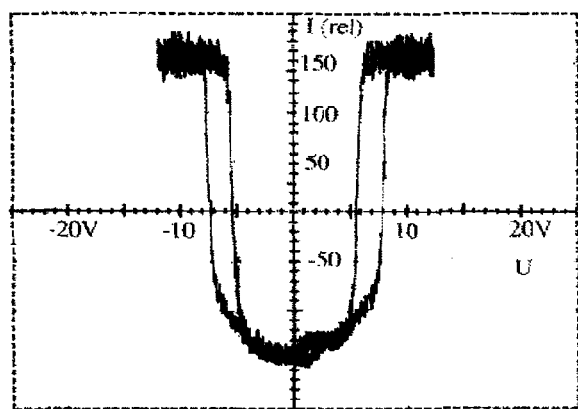


Figure 4. Optical transmittance (I_{rel}) versus the applied electric field (U/V) ($T = 125^{\circ}\text{C}$, $f = 0.1$ Hz).

phase: a current response with two peaks, a double hysteresis loop and three electro-optic states. This behaviour was found to be due to a monostable surface anchoring of liquid crystalline materials with an $S_C^* - N^*$ phase sequence [29]. When cooling from the isotropic to the S_C^* phase in presence of an electric field no stripe texture emerges; instead a uniform layer direction with the usual ferroelectric behaviour results.

Both compounds **9c** and **9d** show selective reflection in the cholesteric phase. The helical pitch is between 290 and 450 nm for **9c**, and 255 and 430 nm for **9d**, with the helix being left-handed in both cases. The temperature-dependence of the pitch and the selective reflection of **9d** are shown in figures 5 and 6.

The use of an additional cyclohexyl ring in the mesogenic unit leads to compound **9e**, which exhibits two smectic phases and a cholesteric phase. The unidentified smectic phase, denoted S_X , is not switchable. The additional cyclohexyl ring increases the transition temperatures. In the cholesteric phase above 270°C , the compound starts to decompose. A 10 mol % mixture of compound **9e** in the host M89/85 shows no ferroelectric properties down to 24°C ; the S_C phase of the host is suppressed (or shifted below room temperature) and the S_A phase is enlarged ($< 24^{\circ}\text{C}$ S_A 109°C N^* 123°C I).

Compounds **17** and **26** exhibit only a smectic A phase and therefore the induced spontaneous polarizations were measured in the host M89/85. In accordance with theoretical predictions the *trans*-configured oxirane induces a lower spontaneous polarization (1.2 nC cm^{-2}) than the *cis*-configured oxirane (8.3 nC cm^{-2}), as shown in figures 7 and 8.

Therefore the structure of both the mesogenic core and the chiral moiety strongly influence the mesomorphic behaviour. Compounds **9a–b** containing two ring cores form no liquid crystals and have relatively low melting points. Addition of one further benzene ring

leads to the mesomorphic compounds **9c** and **9d**. The use of four ring mesogenic cores, as in compound **9e**, has the consequence of high transition temperatures.

Compound **9a** stabilises the S_C^* , S_A and N^* phases of the mixture, whereas in **9e** the S_C^* phase is completely eliminated. There is no explanation for this behaviour at the moment. **9c** and **9d** exhibit relatively high P_S values compared with MHOPBC ($P_S = 100 \text{ nC cm}^{-2}$) [3] and the unbranched compounds **17** and **26**. The additional steric hindrance seems to impede the rotation of the molecules about the longitudinal axis as expected.

5. Conclusions

In an effort to improve the properties of ferroelectric materials, several novel compounds containing the 3,4-epoxy-2-oxyloxy carbonyl unit were synthesized and evaluated. The effect of a third chiral centre adjacent to the epoxide ring on the physical properties in the liquid crystals formed has been investigated.

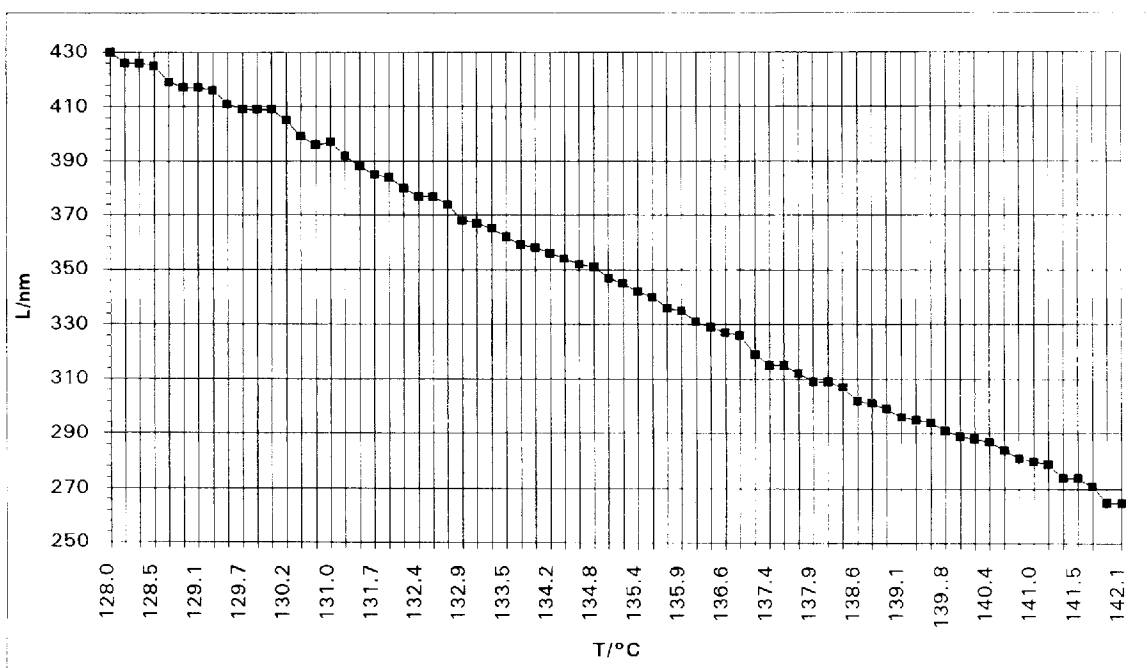
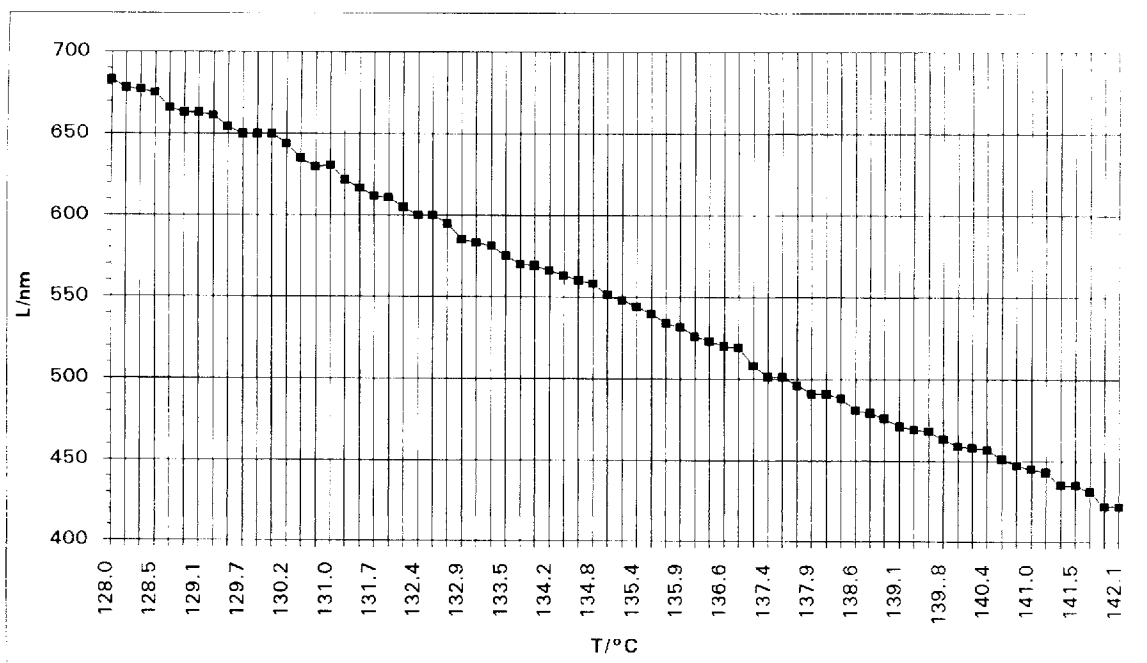
The compounds **9a** and **9b** are not liquid crystalline, but **9a** is a useful chiral dopant to induce a spontaneous polarization.

Using the same mesogenic core as in MHPOBC led to the ferroelectric materials **9c** and **9d** with seemingly antiferroelectric behaviour. The additional chiral oxirane unit in the *cis*-configuration leads to an increased steric hindrance and seems to suppress the herringbone formation of the MHPOBC molecules and therefore the existence of the S_{CA}^* phase.

The chiral methyl branching adjacent to the oxirane ring seems to be necessary for the formation of an S_C^* phase. In compounds **17** and **26**, both with an unbranched epoxy-alkyl chain, only the smectic A phase appears.

6. Experimental

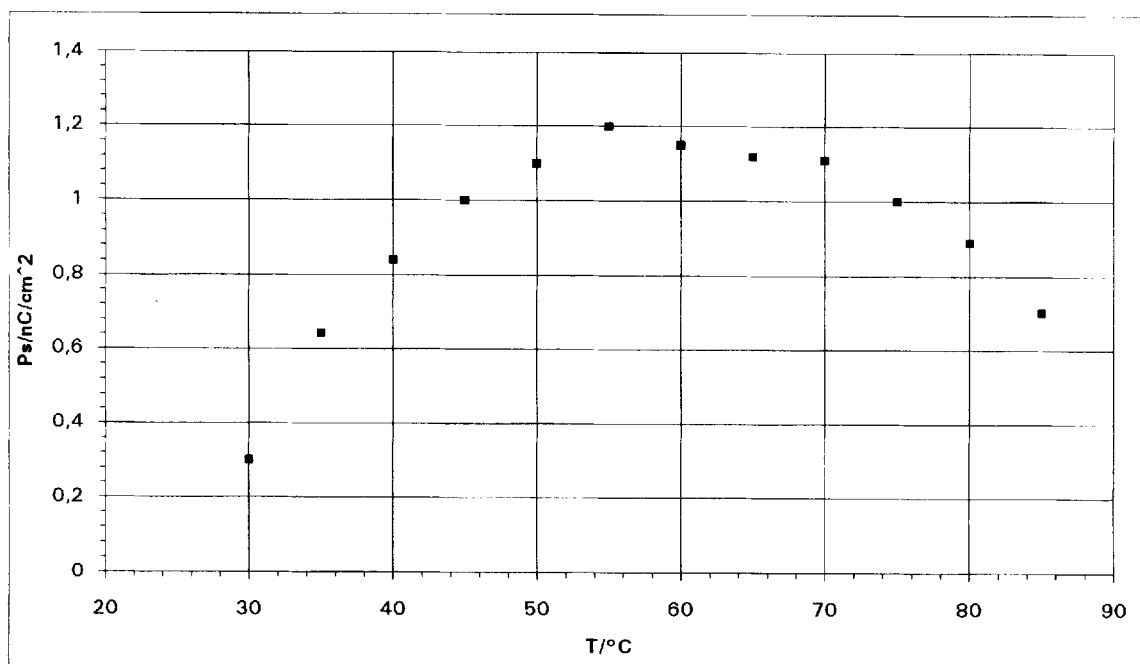
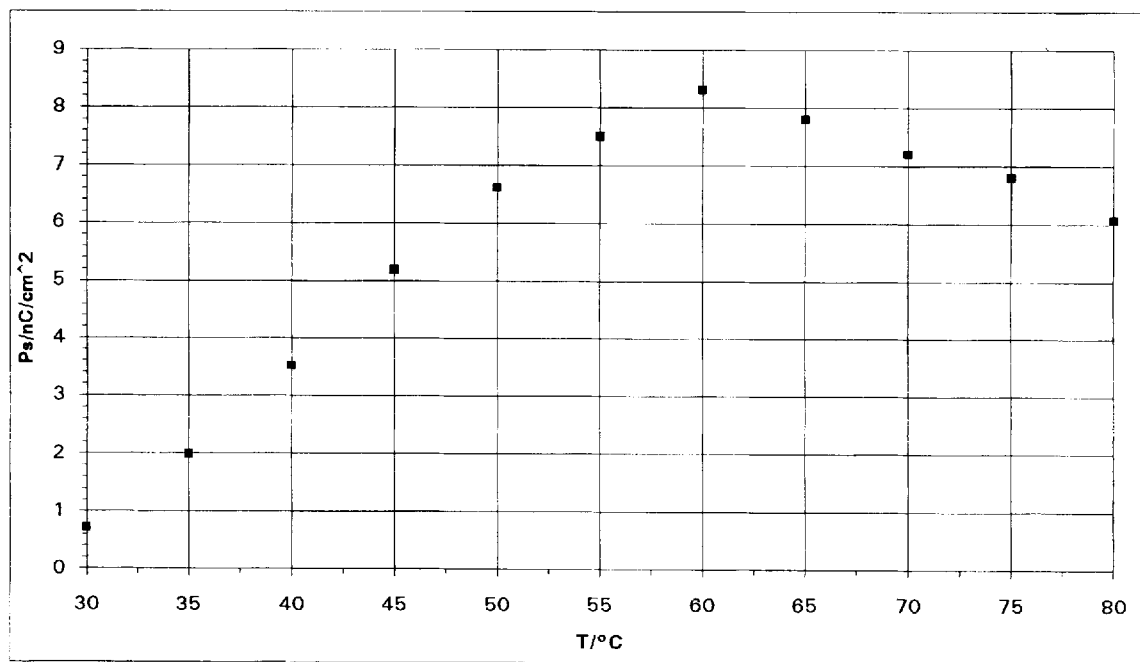
Chemical structures were proved by ^1H NMR spectroscopy (Bruker AM 400, 400 MHz using CDCl_3 as internal standard) and mass spectroscopy (MS, Varian MAT 711). Specific optical rotations were measured using a Perkin-Elmer PE 141 polarimeter; chloroform was used as solvent. Melting points and transition temperatures of the mesophases were observed by a Jenapol polarizing microscope in conjunction with a hot stage and a temperature controlling unit (Linkam THM 600 and Linkam TMS 90). Tilt angles and spontaneous polarizations were measured in 2 or $4 \mu\text{m}$ thick cells, coated with unidirectionally rubbed polyimide alignment layers. Purifications were performed using flash chromatography (Merck silica gel, $15\text{--}30 \mu\text{m}$). Final products were further purified by MPLC (Büchi) and thereafter recrystallized, using ethanol as solvent. The enantiomeric excesses of the final substances were at least 90%, as the other diastereomer was not detectable by ^1H NMR spectroscopy.

Figure 5. Temperature dependence of the pitch of **9d**.Figure 6. Temperature dependence of the selective reflectance of **9d**.

6.1. (1*S*,2*S*,3*S*)-(+)4-(2,3-Epoxy-1-methylheptyloxy-carbonyl)phenyl 4-octyloxybenzoate (**9a**)

477 mg (1.80 mmol) of the phenol **8** were esterified to yield 370 mg (41%) of a colourless solid. $[\alpha]_D^{25} = +44^\circ$ ($c = 1.51$ in CHCl_3). $^1\text{H NMR}$ (CDCl_3): $\delta = 0.90$ (t, $J = 7$ Hz, 3H), 0.95 (t, $J = 7$ Hz, 3H), 1.23–1.74 (m, 16H),

1.43 (d, $J = 6$ Hz, 3H), 1.82 (quint, $J = 7$ Hz, 2H), 3.06 (dt, $J = 7$ and 4 Hz, 1H), 3.16 (dd, $J = 9$ and 4 Hz, 1H), 4.05 (t, $J = 7$ Hz, 2H), 5.02 (dq, $J = 9$ and 6 Hz, 1H), 6.97/8.13 (AA'BB', $J = 9$ Hz, 4H), 7.29/8.15 (AA'BB', $J = 9$ Hz, 4H). MS (40°C): m/e 496 (3.5%, M^-), 353 (3.5), 233 (100), 121 (34), 107 (4), 93 (5), 69 (6), 55 (6).

Figure 7. Temperature dependence of the induced spontaneous polarization of **16**.Figure 8. Temperature dependence of the induced spontaneous polarization of **26**.

6.2. (1*S*,2*S*,3*S*)-(+)-4-(2,3-Epoxy-1-methylheptyloxy-carbonyl)phenyl 2-octyloxy-pyridine-5-carboxylate (**9b**)

50 mg (0.18 mmol) of the phenol **8** were esterified to yield 48 mg (51%) of a colourless solid. $[\alpha]_D^{25} = +41^\circ$ ($c = 1.52$ in CHCl_3). $^1\text{H NMR}$ (CDCl_3): $\delta = 0.87$ (t, $J =$

7 Hz, 3H), 0.94 (t, $J = 7$ Hz, 3H), 1.21–1.73 (m, 16H), 1.79 (quint, $J = 7$ Hz, 2H), 1.43 (d, $J = 7$ Hz, 3H), 3.06 (dt, $J = 7$ and 5 Hz, 1H), 3.18 (dd, $J = 9$ and 5 Hz, 1H), 4.00 (t, $J = 7$ Hz, 2H), 5.01 (dq, $J = 9$ and 7 Hz, 1H), 6.60/7.95/8.34 (ABC, $J_{AB} = 10$ Hz, $J_{BC} = 3$ Hz, 3H),

7.25/8.15 (AA'BB', $J = 8.5$ Hz, 4H). MS (130°C): m/e 497 (6%, M⁺), 354 (5), 234 (100), 149 (4), 135 (2), 122 (20), 94 (2), 69 (2), 55 (7).

6.3. (1*S*,2*S*,3*S*)-(+) -4-(2,3-Epoxy-1-methylheptyloxy-carbonyl)phenyl 4'-decyloxybiphenyl-4-carboxylate (**9c**)

273 mg (1.03 mmol) of the phenol **8** were esterified to yield 130 mg (21%) of a colourless solid. $[\alpha]_D^{26} = +8^\circ$ ($c = 1.43$ in CHCl₃). ¹H NMR (CDCl₃): $\delta = 0.89$ (t, $J = 7$ Hz, 3H), 0.95 (t, $J = 7$ Hz, 3H), 1.18–1.73 (m, 20H), 1.44 (d, $J = 6$ Hz, 3H), 1.82 (quint, $J = 7$ Hz, 2H), 3.07 (dt, $J = 7$ and 5 Hz, 1H), 3.19 (dd, $J = 9$ and 5 Hz, 1H), 4.01 (t, $J = 7$ Hz, 2H), 5.03 (dq, $J = 9$ and 6 Hz, 1H), 7.00/7.60 (AA'BB', $J = 8.5$ Hz, 4H), 7.35/8.17 (AA'BB', $J = 8.5$ Hz, 4H), 7.70/8.23 (AA'BB', $J = 8.5$ Hz, 4H). MS (150°C): m/e 600 (5%, M⁺), 457 (1), 337 (100), 264 (1), 197 (12), 149 (18), 121 (24), 99 (20), 57 (80).

6.4. (1*S*,2*S*,3*S*)-(+) -4-(2,3-Epoxy-1-methylheptyloxy-carbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (**9d**)

103 mg (0.39 mmol) of the phenol **8** were esterified to yield 50 mg (22%) of a colourless solid. $[\alpha]_D^{24} = +9.4^\circ$ ($c = 1.80$ in CHCl₃). ¹H NMR (CDCl₃): $\delta = 0.90$ (t, $J = 7$ Hz, 3H), 0.95 (t, $J = 7$ Hz, 3H), 1.24–1.73 (m, 16H), 1.44 (d, $J = 7$ Hz, 3H), 1.82 (quint, $J = 7$ Hz, 2H), 3.07 (dt, $J = 7$ and 5 Hz, 1H), 3.19 (dd, $J = 9$ and 5 Hz, 1H), 4.02 (t, $J = 7$ Hz, 2H), 5.03 (dq, $J = 9$ and 7 Hz, 1H), 7.01/7.60 (AA'BB', $J = 9$ Hz, 4H), 7.32/8.17 (AA'BB', $J = 9$ Hz, 4H), 7.70/8.24 (AA'BB', $J = 9$ Hz, 4H). MS (300°C): m/e 572 (4%, M⁺), 446 (1), 429 (3), 309 (100), 197 (10), 141 (2), 121 (4), 55 (10).

6.5. (1*S*,2*S*,3*S*)-(+) -4-(2,3-Epoxy-1-methylheptyloxy-carbonyl)phenyl 4'-(4"-pentylcyclohexyl)biphenyl-4-carboxylate (**9e**)

172 mg (0.65 mmol) of the phenol **8** were esterified to yield 200 mg (52%) of a colourless solid. $[\alpha]_D^{26} = +9^\circ$ ($c = 1.24$ in CHCl₃). ¹H NMR (CDCl₃): $\delta = 0.90$ (t, $J = 7$ Hz, 3H), 0.95 (t, $J = 7$ Hz, 3H), 1.00–1.73 (m, 19H), 1.44 (d, $J = 6$ Hz, 3H), 1.92 (td, $J = 12$ and 3 Hz, 4H), 2.54 (tt, $J = 12$ and 3 Hz, 1H), 3.07 (dt, $J = 7$ and 5 Hz, 1H), 3.19 (dd, $J = 9$ and 5 Hz, 1H), 5.02 (dq, $J = 9$ and 6 Hz, 1H), 7.32/7.60 (AA'BB', $J = 8$ Hz, 4H), 7.34/8.25 (AA'BB', $J = 8.5$ Hz, 4H), 7.73/8.17 (AA'BB', $J = 8.5$ Hz, 4H). MS (250°C): m/e 596 (5%, M⁺), 580 (0.2), 453 (3), 422 (1.5), 364 (16), 33 (100), 251 (6), 238 (8), 121 (10), 69 (12), 55 (18).

6.6. (2*S*,3*R*)-(–) -4-(2,3-Epoxyoctyloxy-carbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (**17**)

2.36 g (8.92 mmol) of the phenol **16** were esterified to yield 1.63 g (34%) of a colourless solid. $[\alpha]_D^{28} = -5.4^\circ$ ($c = 2.22$ in CHCl₃). ¹H NMR (CDCl₃): $\delta = 0.89$ (t, $J = 7$ Hz, 3H), 0.90 (t, $J = 7$ Hz, 3H), 1.24–1.64 (m, 18H),

1.82 (quint, $J = 7$ Hz, 2H), 2.95 (dt, $J = 5$ and 2 Hz, 1H), 3.11 (ddd, $J = 6, 3$ and 2 Hz), 4.02 (t, $J = 7$ Hz, 2H), 4.21/4.62 (ABd, part A: $J = 12$ and 6 Hz, 1H, part B: $J = 12$ and 3 Hz, 1H), 7.01/7.60 (AA'BB', $J = 9$ Hz, 4H), 7.34/8.16 (AA'BB', $J = 9$ Hz, 4H), 7.70/8.24 (AA'BB', $J = 9$ Hz, 4H). MS (250°C): m/e 572 (5%, M⁺), 429 (1), 309 (100), 197 (10), 121 (16), 97 (10), 83 (12), 69 (18), 57 (38), 55 (40).

6.7. (2*S*,3*R*)-(+) -4-(2,3-Epoxyoctyloxy-carbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (**26**)

1.09 g (4.02 mmol) of the phenol **25** and 1.31 g (4.02 mmol) 4-octyloxybiphenyl-4'-carboxylic acid, were esterified to yield 921 mg (40%) of a colourless solid. $[\alpha]_D^{29} = +4.4^\circ$ ($c = 2.22$ in CHCl₃). ¹H NMR (CDCl₃): $\delta = 0.89$ (t, $J = 6$ Hz, 3H), 0.91 (t, $J = 6$ Hz, 3H), 1.24–1.67 (m, 16H), 1.82 (quint, $J = 6$ Hz, 2H), 3.09 (td, $J = 6$ and 4 Hz, 1H), 3.34 (dt, $J = 7$ and 4 Hz, 1H), 4.02 (t, $J = 6$ Hz, 2H), 4.32/4.60 (ABd, part A: $J = 12$ and 7 Hz, 1H, part B: $J = 12$ and 4 Hz, 1H), 7.01/7.60 (AA'BB', $J = 9$ Hz, 4H), 7.34/8.18 (AA'BB', $J = 9$ Hz, 4H), 7.70/8.24 (AA'BB', $J = 9$ Hz, 4H). MS (220°C): m/e 572 (10%, M⁺), 429 (2), 309 (100), 197 (8), 121 (6), 97 (10), 83 (18), 70 (40), 57 (42).

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