This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 19 February 2013, At: 11:49
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Ferroelectric Liquid Crystals Containing the Chiral Oxirane Carboxylic Ester Unit Positioned Terminally to or Inside of the Mesogenic Part

G. Scherowsky [a], J. Gay [a] & N. K. Sharma [a b]

[a] Institut für Organische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-1000, Berlin, 12, F. R. G.

[b] University of Jammu, Jammu, Tawi, 180004, India

Version of record first published: 04 Oct 2006.

To cite this article: G. Scherowsky , J. Gay & N. K. Sharma (1990): Ferroelectric Liquid Crystals Containing the Chiral Oxirane Carboxylic Ester Unit Positioned Terminally to or Inside of the Mesogenic Part, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 178:1, 179-192

To link to this article: http://dx.doi.org/10.1080/00268949008042718

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1990, Vol. 178, pp. 179–192
Reprints available directly from the publisher
Photocopying permitted by license only
© 1990 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

Ferroelectric Liquid Crystals Containing the Chiral Oxirane Carboxylic Ester Unit Positioned Terminally to or Inside of the Mesogenic Part*

G. SCHEROWSKY, J. GAY, and N. K. SHARMA†

Institut für Organische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12 F. R. G., †University of Jammu, Jammu Tawi–180004, India.

(*Received October 28, 1988; in final form July 21, 1989*)

The synthesis, phase behaviour, spontaneous polarization and response times of a new class of chiral LCs of general structure 6,7, possessing a (2R, 3S)-2-oxirane carboxylic acid unit connected with mesogenic building blocks are described. Several of the new compounds exhibit ferroelectric LC phases (S_c*). First examples of ferroelectric LCs having the chriral unit incorporated in the mesogenic moiety are described. They show better mesomorphic properties (broader S_c*-phases) compared with analogous compounds bearing the chiral unit terminally. Some of the new compounds are useful as dopants to induce ferroelectric properties in LCs possessing S_c-phases. The ester group adjacent to the oxirane ring increases the chemical stability of the three membered ring system.

Keywords: Ferroelectric liquid crystals, chiral oxirane carboxylic esters

INTRODUCTION

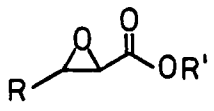
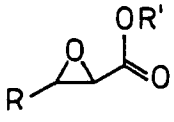
Ferroelectricity in LCs, first postulated and soon afterwards experimentally demonstrated by Meyer,[1] now attracts great interest in both fundamental research and in technological applications. A basic understanding of the origin of the spontaneous polarization and correlations between molecular structure of chemical substances and ferroelectric properties of their smectic LC phases have yet to be developed. First steps towards this objective have been done[2–4] and some guidelines in the design of ferroelectric LCs have been given. The idea to unwind the helical superstructure of S_c*-phase e.g. in thin cells by surface forces,[5] resulting in a polarized sample with macroscopic ferroelectric polarization was an important approach towards technological application of such materials. Fast switching bistable electrooptical devices based on this principle, are under investigation. There is a need for new ferroelectric LC materials possessing high spontaneous polarization, low rotational viscosity and a broad S_c*-phase range about room temperature.[6,7]

*Presented in part at the First International Symposium on Ferroelectric Liquid Crystals in Bordeaux-Arcachon, September, 21–23, 1987.

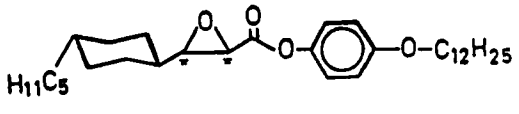
Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

The magnitude of the spontaneous polarization is related to the lateral dipole moment near the chiral centre of the LC molecule. Polar groups directly attached to the stereogenic centre have been shown to increase the spontaneous polarization.[4,8] To incorporate a chiral oxirane ring into a smectic LC seemed to be an idea to achieve a high polarization density. Because of the conformational rigidity of this ring system an averaging of the lateral dipole should be reduced. The first example of a ferroelectric LC containing a nonracemic 2,3-epoxy alcohol was published by Walba.[9] Independently we tested the idea to incorporate a chiral 2-oxirane carboxylic ester unit in a smectogenic LC molecule.[10]

There are two reasons which favour epoxides having a carboxylic function adjacent to the three membered ring system. First, the chemical stability of the oxirane ring is enhanced,[11] second the lateral dipole moment caused by the oxirane ring should be increased by the carbonyl neighbour group. In oxirane carboxylic esters there are two preferred conformations A and B in which the carbonyl group is located syn or anti to the oxirane ring.[12]

A  B 

In A the two dipoles of the oxirane ring and the carbonyl group enhance each other, in B they compensate each other partially. 2-Oxirane carboxylic esters mostly exhibit two separated IR carbonyl bands. Due to a preference for conformer A in the equilibrium, the carbonyl band at higher frequency is stronger. To examine whether this phenomenon is also to be observed in LC solutions, we measured the IR-spectra of *6a* in the nematic phase of RO-TN 404 and in the S_c-phase of 9 (see Table III).

6a 

In both LC phases 6a shows two carbonyl bands at 1760 and 1740 cm^{-2} (see Figure 1). The higher extinction of the band at 1760 cm^{-2} demonstrates, that conformation A is favoured in which the carbonyl group enhances the oxirane dipole in 6a. One goal of the present work was to use this knowledge in the design of LCs with ferroelectric properties and high spontaneous polarization. Connecting a chiral oxirane carboxylic acid unit with an appropriate smectogenic building block should lead to this goal.

Up to now all LCs exhibiting S_c*-phases contain the chiral centre in the terminal tail unit.[4,13] Recently compounds bearing a chiral lactate group between two mesogenic moieties have been synthesized yielding valuable dopants for induced ferroelectric LC phases with extrapolated high values of spontaneous polarization. Those compounds however did not show any LC behaviour.[14] A second goal of

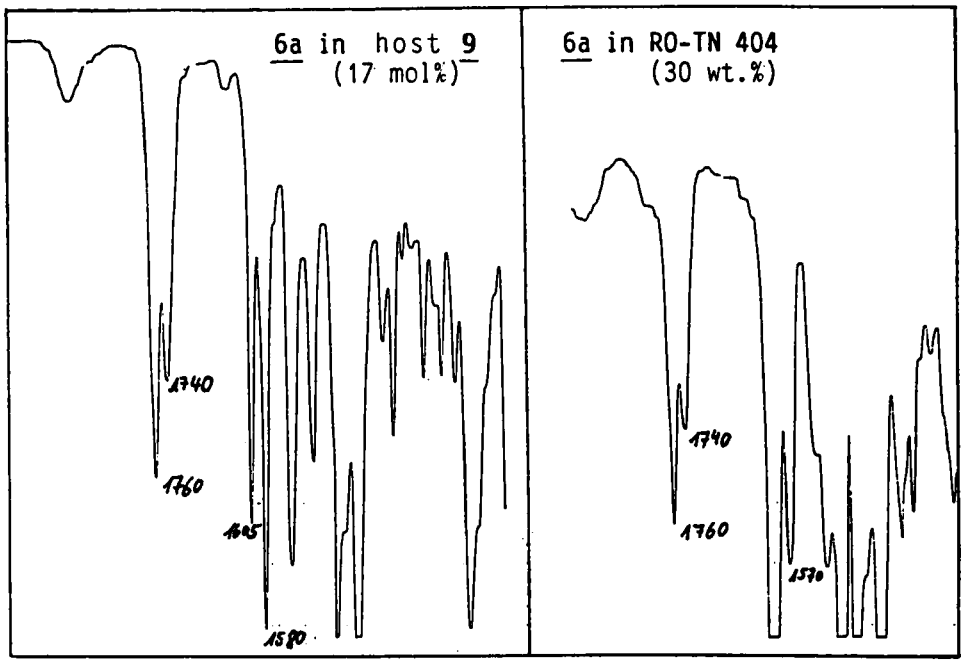
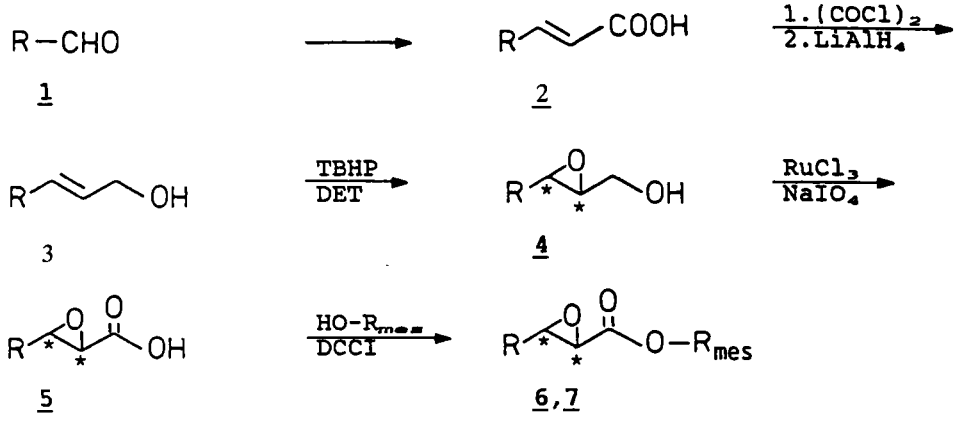


FIGURE 1 In both LC phases 6a shows two carbonyl bands at 1760 and 1740 cm^{-1}. The higher extinction of the band at 1760 cm^{-1} demonstrates, that conformation A is favoured in which the carbonyl group enhances the oxirane dipole in 6a.

our work was to find out whether an incorporation of the chiral oxirane carboxylic ester moiety within the mesogenic part would result in liquid crystals exhibiting S_c*-phases. A further aim was to find combinations of smectogenic building blocks and the chiral unit which would lead to broad S_c*-phases.

SYNTHESIS

Scheme 1:



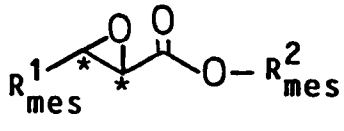
Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

LCs containing the chiral oxirane ester unit between two mesogenic moieties were synthesized starting from mesogenic aldehydes 1. Condensation with malonic acid and subsequent decarboxylation transformed 1 into unsaturated carboxylic acids 2. Reduction of the acid chlorides with lithium aluminum hydride gave the allylic alcohols 3. Sharpless epoxidation[15] afforded the (*S*,*S*)-epoxy alcohols 4. The enantiomeric excess in compounds 4 was determined by derivatization with α-methoxy-α-(trifluoromethyl)-phenyl-acetic acid (Mosher reagent[16]) and 400 MHz ^{1}H-NMR analysis of the ratio of diastereomers formed. The epoxy alcohols 4 were oxidized to the 2-oxirane carboxylic acids 5 using $RuCl_3/NaIO_4$.[17] Esterification of the latter with phenols was accomplished by the Steglich method[18] affording the esters$_6$ a-g (Table I). Oxirane carboxylic esters 7a-f bearing only one mesogenic unit located at the ester function and having a *n*-octyl chain at C-3 were synthesized starting from 1-nonanal 1a in the same reaction sequence as outlined in Scheme 1.

PHASE BEHAVIOUR

Phase transition temperatures and phase types given by compounds 6a-g and 7a-f are presented in Table I and II. Phases are identified by textural observations. Compound 6a exhibits only a monotropic S_A-phase. Incorporation of a second cyclohexyl ring in R^1_{mes} (6e-g) results in enantiotropic S_A- and S_B-phases, and in the case of compound 6e exhibits an additional cholesteric phase. Enlarging R^2_{mes} by a second aromatic ring (6b) results in a sequence of four LC phases, including a S_c*-phase and a blue phase. Using 2-octylthio-4-phenyl-pyrimidine as R^2_{mes}—a mesogenic group recently shown to exhibit S_c-phases—only shows a S_A-phase. Incorporation of a third aromatic ring in R^2_{mes} (connected by an ester linkage to the biphenyl system) 6d, results in a phase sequence, comprising a broad S_c*-phase over a temperature range of 95°. Compounds 6e-g show a decreasing mesophase range with increasing length of the terminal alkyl chain. Compounds 7a-e (Table II), having only one mesogenic unit connected with the oxirane ring system, show a distinct smaller range of mesophases compared with analogues having two mesogenic units (6b/7c, 6d/7e). Compounds 7a and 7b have very small S_c*-phases, and compound 7c shows no S_c*-phase but a S_E-phase.

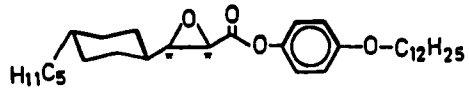
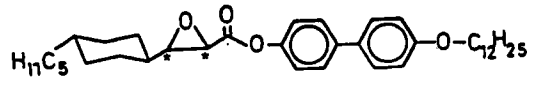
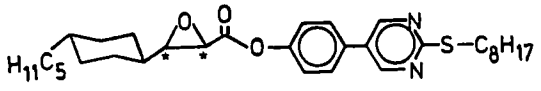
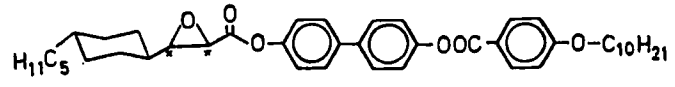


SPONTANEOUS POLARIZATION

The spontaneous polarization was measured in a 10 mol% solution in host 8, in two cases 9 was used (for solubility reasons). The structures and phase sequences of the hosts are given in Table III. The *Ps*-values presented are extrapolated from those obtained in mixtures. Phase sequences and transition temperatures: Table IV.

TABLE I

LC-properties,[a] spontaneous polarization,[b] optical response time (τ) and tilt angle (Θ) of oxirane carbonic esters 6a–6g

	P_s (nC/cm²)
6a  τ: 210 μs 2Θ = 34° Cr 69.0 (S_A 64.3) I	25
6b  Cr 45.0 S_G 97.8 S_C^* 123.3 S_A 152.5 N* 154.4 BP I 154.7 I	34
6c  Cr 68.0 S_A 162.0 I	15
6d  Cr 60.0 S_2 106.0 S_C^* 201.7 N* 268.0 I	17
6e  Cr 52.0 S_B 121.0 S_A 159.7 N* 167.5 I	64
6f  τ: 55 μs 2Θ = 44° Cr 67.0 S_B 127.3 S_A 161.0 I	52
6g  τ: 130 μs 2Θ = 45° Cr 78.0 S_B 123.0 S_A 154.0 I	35

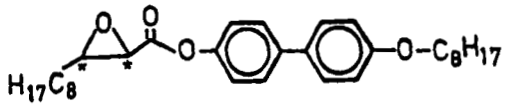
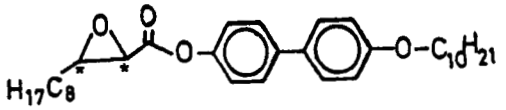
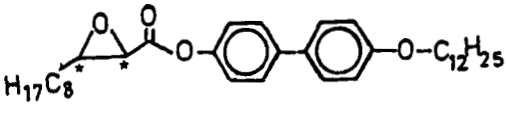
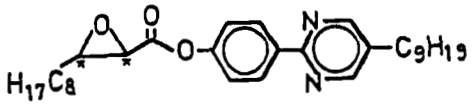
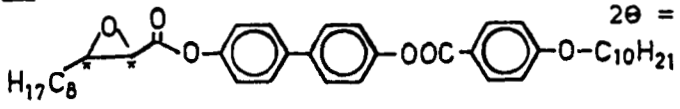
[a]Cr: crystalline; S_A, S_B, S_C^*, S_G, S_2: smectic phases (S_2: unidentified), N*: cholesteric phase; BP: blue phase, I: isotripic liquid (temperatures in °C).

[b]P_s, τ and Θ of all compounds are measured in the matrix 8 (T: 45°C); except compound 6a (measured in 9, T: 20°C)

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

TABLE II

LC-properties,[a] spontaneous polarization,[b] optical response time (τ) and tilt angle (Θ) of oxirane carbonic esters 7a–7e.

	P_s (nC/cm²)
7a  Cr 117.5 S_B 118.7 S_C^* 119.7 I	30
7b  Cr 116.9 S_B 119.4 S_C^* 119.7 I	22
7c  Cr 110.7 S_E 119.0 I	10
7d τ: 80 µs 2Θ = 40°  Cr 55.8 (S_B 41.1; S_C^* 54.4) S_A 64.6 N^* 65.9 I	65
7e τ: 80 µs 2Θ = 30°  Cr 108.0 S_2 127.0 S_C^* 187.0 N^* 205.0 I	78

[a]See Table I.

[b]P_s, τ and Θ of all compounds are measured in the matrix 8 (T: 45°C); except compound 7d (measured in 9, T: 20°C).

DISCUSSION

For those compounds bearing the chiral oxirane unit between two mesogenic moieties the spontaneous polarization increases with elongation either of the aromatic part from phenyl to biphenyl (6a/6b) or the aliphatic part from cyclohexyl to bicyclohexyl (6a/6g). A decrease in P_s is observed by exchanging an alkoxy phenyl for an alkylthio pyrimidine ring in the aromatic part (6b/6c) and, surprisingly, also

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

TABLE III

Structures and phase sequences of the hosts

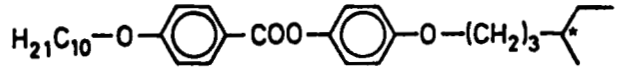
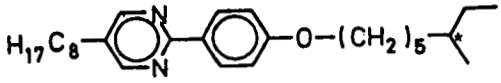
8	
Cr 32 (S_a 20) S_c 70 S_A 132 I	
9	
Cr 13 S_c 49 S_A 57 I	

TABLE IV

Phase sequences and transition temperatures of the mixtures

6a	12 S_c^* 28 S_A 54 I
6b	30.5 S_c^* 68 S_A 76 N^* 78.5 I
6c	29 S_c^* 59 S_A 77 I
6d	25 S_c^* 51.5 S_A 65 N^* 78.5 I
6e	33.5 S_c^* 65.5 S_A 80 I
6f	34.5 S_c^* 64.5 S_A 85 I
6g	31.5 S_c^* 60.5 S_A 77 I
7a	37 S_c^* 72 S_A 76.5 I
7b	37 S_c^* 73 S_A 77 I
7c	37.5 S_c^* 72 S_A 77 I
7d	5 S_c^* 42 S_A 58 I
7e	40 S_c^* 72 S_A 74.5 N^* 81 I

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

by further elongation of the biphenyl part with a benzoate unit (6b/6d). In the series 7a-c a decrease in *Ps* seems to occur with increasing chain length. If one compares compounds 6b and 7c, the location of the oxirane ester unit between two mesogenic moieties (6b) seems to be favourable to obtain a higher induced spontaneous polarization. On the other hand, if the chiral unit is located at one end of the mesogenic moiety, an elongation of the biphenyl system by an alkoxy benzoate, increases the spontaneous polarization distinctly (7b/7e).

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

Experimental Part

^{1}H-NMR: Bruker WM 400.- MS: Varian MAT 711 (70 eV).- IR: Perkin Elmer PE 225 or PE 257.- Specific optical rotation: Perkin Elmer PE 241 polarimeter.- Texture observations: Leitz polarising microscope and Mettler FPZ heating stage.- Measurements of spontaneous polarization: in test cells with a spacing of 2μ or 4μ. The glass substrates of the cells were coated with polyimide and both substrates were rubbed. The cells were filled by capillary action and were thermostated during the measurements in a Mettler heating stage FP 82. Spontaneous polarization was obtained by the Diamant bridge:[19] applied voltage: 5-20 V, frequency: 50–100 Hz. Response time (τ) was determined by applying a rectangular wave of ± 10 V/μm and is defined as time difference between voltage reversal and 90% change in optical transmission. Phase transitions were determined using a Perkin Elmer DSC 2 apparatus. Chromatographic purifications were performed using flash chromatography (FC) on ICN Biomedicals silica (32-63μ).

Elemental analysis: Microanalytical department of the Institut of Organic Chemistry.

Petroleum ether(PE): b.p. 40–60°C.

(2S, 3S)-(-)-3-[*trans*-4-(*trans*-4-pentylcyclohexyl)-cyclohexyl]-2,3-epoxy-propanol 4a

A 50 ml round-bottom flask is oven-dried, then fitted with a serum cap, and flushed with nitrogen. The flask is charged with dry dichloromethane (20 ml) and cooled by stirring in a −23°C bath (dry ice/acetone). Then the following liquids are added sequentially while stirring in the cooling bath: 0.88 ml titanium tetraisopropoxide (0.86 g, 3 mmol), 0.52 ml *L*-(+)-diethyl tartrate (*L*-(+)-DET; 0.62 g, 3 mmol), the mixture is stirred for 5 min before the next addition of 3-[*trans*-4-(*trans*-4-pentylcyclohexyl)-cyclohexyl]-*E*-2-propenol (0.88 g, 3 mmol) and, finally a *t*-butyl hydroperoxide solution (2.0 ml, 6 mmol; 3.0 molar in toluene). The resulting homogeneous solution is then stored overnight at −23°C in the freezer. Then the flask is placed into a −23°C bath (dry ice/acetone), and an 10% aqueous tartaric acid solution (7.5 ml) is added. While stirring, the aqueous layer solidifies. After 30 min the cooling bath is removed and stirring is continued at room temperature until the aqueous layer becomes clear. After separation, the organic layer is washed once with water and concentrated.

The residue is diluted with ether (40 ml), the resulting solution is cooled in an ice bath, and then 1*N* sodium hydroxide solution (9 ml) is added. This two-phase mixture is stirred at 0°C for 30 min. The ether phase is washed with brine and dried

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

($MgSO_4$). FC with PE/ether (4:1 → 1:1) yielded 0.65 g (70%) of 4a, which was shown to be > 90% enantiomerically pure.

m.p.: 42°C (S_E 167°C I)
$[a]_D^{20} = -20°$ (c 1.2 in $CHCl_3$).-
IR($CHCl_3$):3600,3450 br(OH),1470,1450 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.78-0.90(m;2H),0.88(t,J = 7Hz; 3H),0.90-1.33(m;16H), 1.64(dd,J = 7.5 and 5.5Hz;OH),1.65-1.79(m;9H),1.91(dbr,J = 12HZz;1H), 2.73(dd,J = 6.5 and 2Hz;C*H),2.97(ddd,J = 4.5 2.5 and 2Hz;C*H), 3.61; 3.91(Ab_{dd},J = 13Hz;part A:dd,J = 7.5 and 4.5Hz;part B:dd,J = 5.5 and 2.5Hz; 2H).-
MS/CI(130°C):m/e 309(30%,M + 1), 291(30,M-H_2O + 1),273(34),235(6),73(100,M-$c_{17}H_{31}$),61(36).-
$C_{20}H_{36}O_2$; calcd. C 77.87; H 11.76, found C 77.92; H 11.59.-

(2R,3S)-(-)-3-[*trans*-4-(*trans*-4-pentylcyclohexyl)-cyclohexyl]-2-oxirane-carboxylic-acid 5a

A flask is charged with carbontetrachloride (1.3 ml), acetonitrile (1.3 ml), water (1.4 ml), 4a (200 mg, 0.65 mmol), and sodium metaperiodate (308 mg, 2.2 equiv.). To this biphasic solution ruthenium trichloride hydrate (8 mg, 7.7 mol%) is added, and the mixture is stirred vigorously for overnight at room temperature. Then dichloromethane (10 ml) are added, and the phases are separated. The aqueous phase is extracted three times with dichloromethane, the combined organic extracts are dried ($MgSO_4$) and concentrated. The catalyst can be removed by filtration of an etheral solution through a celite pad. 5a was used for the next step without further purification.
Yield: 0.2 g (95%).

m.p.: dec.
$[\alpha]_D^{20} = -20°$ (c 0.8 in $CHCl_3$)
IR(KBr):1710,1740(CO),1450 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.77-0.91(m;2H),0.88(t,J = 7Hz;3H),0.91-1.19(m;9H),1.19-1.34(m;10H),1.68(dbr,J = 12Hz;2H),1.74(dbr,J = 12Hz;2H), 1.78(dbr,J = 12Hz;3H), 1.90(dbr,J = 12Hz;1H),3.00(dd,J = 6.5 and 2Hz;C*H),3.33(d,J = 2Hz;C*H).-
MS(170°C):m/e 322(6%,M^+),304(12,M-H_2O),278(26),260(10), 247(15), 234(56),163(18),137(32),109(40),97(92),83(100),55(76).

GENERAL PROCEDURE FOR ESTERIFICATION

A solution of carboxylic acid (10 mmol), *N*,*N*-dicyclohexyl-carbodiimid (11 mmol), the hydroxy compound (11 mmol) and 4,4-dimethylaminopyridine (1 mmol) in dry dichloromethane (25 ml) is stirred at room temperature overnight. The *N*,*N*-dicyclohexylurea is filtered off and the filtrate washed with water, dried ($MgSO_4$) and concentrated. Products are purified by FC with PE/dichloromethane (4:1 → 1:1).

(2R,3S)-(-)-4-dodecyloxyphenyl-3-(*trans*-4-pentylcyclohexyl)-oxirane-2-carboxylate 6a

mm.p.: 69°C
$[\alpha]_D^{20}$ = −28° (c 1.4 in $CHCl_3$).-
IR(CCl_4):1775,1755(CO),1600(Ar),1505 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.89(t,J=7Hz;3H),0.90(t,J=7Hz;3H),0,90-0.97(m;2H),1.13-1.39(m;28H,1.44(quint,J=7Hz;2H),1.77(quint,J=7Hz;2H),1.83 (dbr,J=12Hz;3H),1.91 (dbr, J=12Hz;1H),3.13(dd,J=6 and 2Hz;C*H),3.48 (d, J=2Hz;C*H),3.92(t,J=6.5Hz;2H),6.87;7.02(AA'BB',J=9Hz;4H).-
MS(130°C):m/e 501(31%,M+1),500(86,M^+),278(40,$C_{18}H_{30}O_2$), 110(100,$C_6H_6O_2$),57(48).-
$C_{32}H_{52}O_4$; calcd. C 76.75; H 10.47, found C 77.20; H 10.56.-

(2R,3S)-(-)-4'-(dodecyloxybiphenyl-4-yl)-3-(*trans*-4-pentylcyclohexyl)-oxirane-2-carboxylate 6b

m.p.: 45°C
$[\alpha]_D^{20}$ = −24° (c 1.2 in $CHCl_3$).-
IR(KBr):1755 br(CO),1600 cm^{-1}(ar).-
^{1}H-NMR($CDCl_3$):δ 0.89(t,J=7Hz;3H),0.90(t,J=7Hz;3H)0.90-0.98 (m;2H),1.15-1.41(m;28H),1.46(quint,J=7Hz;2H),1.80(quint, J=7Hz;2H),1.83(dbr;3H),1.93 (dbr,J=12Hz;1H),3.17(dd,J=6 and 2Hz;C*H),3.52(d,J=2Hz; C*H), 3.99(t,J=6.5Hz;2H),6.96;7.48 (AA'BB',J=8.5Hz;4H),7.17;7.54 (AA'BB', J=8.5Hz;4H).-
MS(170°C):m/e 576(6%,M^+),354(77,$C_{24}H_{34}O_2$),186(100, $C_{12}H_{10}O_2$),55(18).-
$C_{38}H_{56}O_4$;calcd. C 79.13; H 9.79, found C 79.09; H 9.77.-

(2R,3S)-(-)-4-(2-octylthiopyrimidine-5-yl)-phenyl-3-(*trans*-4-pentylcyclohexyl)-oxirane-2-carboxylate 6c

m.p.: 68°C
$[\alpha]_D^{20}$ = −27° (c 1.0 in $CHCl_3$).-
IR($CHCl_3$):1770,1755(CO),1585(ar),1410 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.83-0.96(m;2H),0.87(t,J=7Hz;3H),0.88(t,J=7Hz;3H),1.14-1.40(m;20H),1.47(quint,J=7Hz;2H),1.76(quint,J=7Hz;2H), 1.83(dbr,J=11Hz;3H),1.93(dbr,J=12Hz;1H),3.17(dd,J=6 and 2Hz;C*H), 3.53(d,J=2Hz;C*H),7.26;7.55(AA'BB',J=9Hz;4H),8.71(s;2H).-
MS(235°C):m/e 538(98%,M^+),506(100,M-H_2O-CH_3),491(83),453(17),440(42), 426(62),421(34),316(20,$C_{18}H_{24}N_2OS$),283(18),269(16),218(28), 204(86,$C_{10}H_8N_2OS$),146(30),55(70).-
$C_{32}H_{46}N_2O_3S$; calcd. C 71.34; H 8.61; N 5.20, found C 70.99; H 8.47; N 5.21.-

(2R,3S)-(-)-[4-(4-decyloxybenzoyloxy)-biphenyl-4'-yl]-3-(*trans*-4-pentylcyclohexyl)-oxirane-2-carboxylate 6d

m.p.: 60°C
$[\alpha]_D^{20}$ = −21° (c 0.9 in $CHCl_3$).-

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

IR($CHCl_3$):1760,1730(CO),1610(ar),1510,1490 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.89(t,J = 7Hz;6H),0.90-0.98(m;2H),1.15-1.41(m;24H),
1.48(quint,J = 7Hz;6H),
1.82(quint,J = 7Hz;2H),1.83(dbr,J = 11Hz;3H),1.93(dbr,J = 12Hz;1H),
3.17(dd,J = 6 and 2Hz;C*H),3.53(d,J = 2Hz;C*H),4.05(t,J = 6.5Hz;2H),
7.20;7.59(AA'BB',J = 9Hz4H),7.27;7.59(AA'BB',J = 9Hz;4H),
6.97;8.15(AA'BB',J = 9Hz;4H).-
MS(65°C):m/e 668(0.3%,M^+),550(1.5),446(1.9,$C_{29}H_{34}O_4$),261(100,$C_{17}H_{25}O_2$),
186(4,$C_{12}H_{10}O_2$), 121(52,$C_7H_5O_2$),105(6),55(8).
$C_{43}H_{56}O_6$; calcd. C 77.21; H 8.44, found C 77.21; H 8.45.-

(2R,3S)-(-)-4-heptyloxyphenyl-3-[*trans*-4-(*trans*-4-pentylcyclohexyl)-cyclohexyl]-oxirane-2-carboxylate 6e

m.p.: 52°C
$[\alpha]_D^{20}$ = −25° (c 1.0 in $CHCl_3$).-
IR(KBr):1765,1740(CO),1500 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.78-1.20(m;13H),0.88(t,J = 7Hz;3H),0.89(t,J = 7Hz;3H),1.20-
1.39(m;13H),1.44(quint,J = 7Hz;2H),1.70 (dbr,J = 11Hz;2H),1.73-
1.82(m;5H)1.83(dbr,J = 12Hz;2H),1.93(dbr,J = 12Hz;1H),3.12(dd,J = 6 and
2Hz;C*H),3.47(d,J = 2Hz;C*H),3.92(t,J = 6.5Hz;2H),6.87;7.02
(AA'BB',J = 9Hz;4H).-
MS/CI(330°C):m/e 513(41%,M + 1),512(3,M^+),496(7,M-H-CH_3),306 (12,M-
$C_{13}H_{19}O_2$ + 1),277(46,M-$C_{14}H_{19}O_3$),207(100,$C_{13}H_{19}O_2$),111(21).-
$C_{33}H_{52}O_4$; calcd. C 77.30; H 10.22, found C 77.26; H 10.34.-

(2R,3S)-(-)-4-decyloxyphenyl-3-[*trans*-4-(*trans*-4-heptylcyclohexyl)-cyclohexyl]-oxirane-2-carboxylate 6f

m.p.: 67°C
$[\alpha]_D^{20}$ = −25° (c 1.0 in $CHCl_3$).-
IR(KBr):1770,1750(CO),1600(ar),1510 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.78-1.20(m;13H),o.88(t,J = 7Hz;6H),1.21-1.39
(m;23H)1.44(quint,J = 7Hz;2H),1.70(dbr,J = 11Hz;2H),1.78-1.81(m;5H),
1.83(dbr,J = 12Hz;2H),1.93(dbr,J = 12Hz 1H),3.12(dd,J = 6 and 2Hz;C*H),3.47
(d,J = 2Hz;C*H),3.93)(t,J = 6.5Hz,2H),6.87;7.02(AA'BB',J = 9Hz;4H).-
MS/CI(300°C):m/e 583(80%,M + 1),582(10,M^+),565(12),567(8,M-
CH_3),333(14,$C_{22}H_{37}O_2$),315(22),305(100,$C_{21}H_{37}O$),287(34),251(40),141(28).-
$C_{38}H_{62}O_4$; calcd. C 78.30; H 10.72, found C 78.41; H 10.80.-

(2R,3S)-(-)-4-dodecyloxyphenyl-3-[*trans*-4-(*trans*-4-heptylcyclohexyl)-cyclohexyl]-oxirane-2-carboxylate 6g

m.p.: 78°C
$[\alpha]_D^{20}$ = −25.5° (c 1.0 in $CHCl_3$).-
IR(KBr):1770,1750(CO),1600(ar),1510 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.78-1.20(m;13H),0.89(t,J = 7Hz;6H),1.21-1.39(m;27H),

1.44(quint,J = 7Hz;2H),1.70(dbr,J = 11Hz;2H),1.78-1.83(m;5H),
1.83(dbr,J = 12Hz;2H),1.94(dbr,J = 12Hz;1H) 3.12(dd,J = 6 and 2Hz;C*H),
3.47(d,J = 2Hz;C*H),3.93(t,J = 6.5Hz;2H),6.87;7.02(AA'BB',J = 9Hz;4H).-
MS/CI(340°C):m/e 611(77%,M + 1),610(10,M^+),595(8,M-CH_3),594(18),566(7),
333(14,$C_{22}H_{37}O_2$),315(24,$C_{22}H_{35}O$),305(100,$C_{21}H_{37}O$),287(45),
278(62,$C_{18}H_{30}O_2$),169(24).-
$C_{40}H_{66}O_4$; calcd. C 78.64; H 10.89, found C 79.09; H 10.62.-

(2R,3S)-(-)-(4'-octyloxybiphenyl-4-yl)-3-octyl-oxirane-2-carboxylate 7a

m.p.: 117.5°C
$[\alpha]_D^{20}$ = −21.5° (c 1.0 in $CHCl_3$).-
IR(KBr):1770,1755(CO),1640(ar),1500 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.90(t,J = 7Hz;6H),1.25-1.43(m;18H),1.48(quint,J = 7Hz;2H),
1.51-1.58(m;2H),1.66;1.77(AB_{td},J = 15Hz;part A:td,J = 7 and 6Hz; part B:td,J = 6
and 4.5Hz;2H),1.81(quint,J = 7Hz;2H),3.35(ddd,J = 6,4.5 and 2Hz;C*H),
3.46(d,J = 2Hz;C*H),3.99(t,J = 6.5Hz;2H),6.97;7.48(AA'BB',J = 9Hz;4H),
7.17;7.55(AA'BB',J = 9Hz;4H).-
MS/CI(250°C):m/e 481(20%,M + 1),480(6,M^+),298(8,$C_{20}H_{26}O_2$), 155(100).
$C_{31}H_{44}O_4$;calcd. C 77.46; H 9.23, found C 77.07; H 9.19.-

(2R,3S)-(-)-(4'-decyloxybiphenyl-4-yl)-3-octyl-oxirane-2-carboxylate 7b

m.p.: 116.9°C
$[\alpha]_D^{20}$ = − 17° (c 0.5 in $CHCl_3$).-
IR($CHCl_3$):1750,1740(CO),1610(ar),1500 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.88(t,J = 7Hz;3H),0.89(t,J = 7Hz,3H),1.23-1.42
(m;22H),1.47(quint,J = 7Hz;2H),1.50-1.57(m;2H),1.65;1.77(AB_{td} J = 15Hz;part
A:td,J = 7 and 6Hz;part B:td,J = 6 and 4.5Hz;2H),1.80(quint,J = 7Hz;2H),
3.34(ddd,J = 6,4.5 and 2Hz;C*H),3.46(d,J = 2Hz;C*H),3.99(t,J = 6.5Hz;2H),
6.96;7.48(AA'BB',J = 9Hz;4H),7.16;7.55(AA'BB',J = 9Hz;4H).-
MS(100°C):m/e 508(9%,M^+),326(24,$C_{22}H_{30}O_2$),186(100,$C_{12}H_{10}O_2$),97(8),83(40),
69(72),55(78).-
$C_{33}H_{48}O_4$; calcd. C 77.91; H 9.51, found C 78.33; H 9.61.-

(2R,3S)-(-)-(4'-dodecyloxybiphenyl-4-yl)-3-octyl-oxirane-2-carboxylate 7c

m.p.: 110.7°C
$[\alpha]_D^{20}$ = −10° (c 0.7 in $CHCl_3$).-
IR(KBr):1770,1750(CO),1600(ar),1490 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.91(t,J = 7Hz;3H),0.92(t,J = 7Hz;3H),1.24-1.43
(m;26H),1.48(quint,J = 7Hz;2H),1.52-1.59(m;2H),1.66;1.77(AB_{td} J = 15Hz;part
A:td,J = 7 and 6Hz;part B:td,J = 6 and 4.5Hz;2H)1.81(quint,J = 7Hz;2H),
3.34(ddd,J = 6,4.5 and 2Hz;C*H),3.46(d,J = 2Hz,C*H),3.99(t,J = 6.5Hz;2H),
6.97;7.48(AA'BB',J = 9Hz;4H), 7.17;7.56(AA'BB',J = 9Hz;4H).-
MS(205°C):m/e 536(46%,M^+),354(96,$C_{24}H_{34}O_2$),186(100,$C_{12}H_{10}O_2$),122(13),55(24).-
$C_{35}H_{52}O_4$; calcd. C 78.31; H 9.76, found C 78.45; H 10.00.-

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013

(2R,3S)-(-)-4-(5-nonyl-pyrimidine-2-yl)-phenyl-3-octyl-oxirane-2-carboxylate 7d

m.p.: 55.8°C
$[\alpha]_D^{20} = -21°$ (c 1.0 in $CHCl_3$).-
IR(KBr):1770,1750(CO),1605(ar),1590,1430 cm^{-1}.-
^{1}H-NMR($CDCl_3$):δ 0.89(t,J = 7Hz;3H),0.90(t,J = 7Hz;3H),1.24-1.44(m;22H),1.48-1.60(m;2H),1.61-1.70(m;3H),1.70-1.81(m;1H),2.62(t,J = 7Hz;2H),3.35(ddd,J = 6,5 and 2Hz;C*H),3.46(d,J = 2Hz;C*H),7.25;8.46(AA'BB',J = 9Hz;4H),8.61(s;2H).
MS/CI(.280°C):m/e 481(36%,M + 1),480(2,M^+),299(100,$C_{19}H_{26}N_2O$ + 1),270(6), 155(12).
$C_{30}H_{44}N_2O_3$; calcd. C 74.96; H 9.23; N 5.83, found C 74.73; H 9.34; N 5.82.

(2R,3S)-(-)-[4-(4'-decyloxybenzoyloxy)-biphenyl-4'-yl]-3-octyl-oxirane-2-carboxylate 7e

m.p.: 108°C
$[\alpha]_D^{20} = -14.5°$ (c 2.0 in $CHCl_3$).
IR(KBr):1760,1730 (CO),1605(ar),1510,1490 cm^{-1}.
^{1}H-NMR($CDCl_3$):δ 0.89(t,J = 7Hz;3H),0.90(t,J = 7Hz;3H),1.23-1.43 (m;22H),1.48(quint,J = 7Hz;2H),1.51-1.57(m;2H),1.66;1.77(AB_{id},J = 15Hz; part A:td,J = 7 and 6Hz; part B:td,J = 6 and 4.5Hz;2H),1.83(quint,J = 7Hz;2H), 3.35(ddd,J = 6,4.5 and 2Hz;C*H), 3.47(d,J = 2Hz;C*H),4.05(tJ = 6.5Hz;2H), 7.21;7.60(AA'BB',J = 9Hz;4H),7.60,7.27(AA'BB',J = 9Hz;4H),6.98;8.16 (AA'BB',J = 9Hz;4H).-
MS/CI(250°C):m/e 629(13%,M + 1),628(4,M^+),447(20,$C_{29}H_{34}O_4$ + 1), 261(26,$C_{17}H_{25}O_2$),247(100,$C_{16}H_{22}O_2$ + 1),229(50),155(52),117(46),87(40).71(36).-
$C_{40}H_{52}O_6$; calcd. C 76.40; H 8.34, found C 76.24; H 8.47.-

References

1. R. B. Meyer, L. Liebert, L. Strzelecki and P. Keller, *J. Phys.***36**, L-69 (1975).
2. J. W. Goodby, E. Chin, T. M. Leslie, J. M. Geary and J. S. Patel, *J. Am. Chem. Soc.*, **108**, 4729 (1986).
3. J. W. Goodby, E. Chin, *J. Am. Chem. Soc.*, **108**, 4736 (1986).
4. D. M. Walba, S. C. Slater, W. M. Thurmes, N. A. Clark, M. A. Handschy and F. Supon, *J. Am. Chem. Soc.*, **108**, 5210 (1986).
5. N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
6. M. A. Handschy and N. A. Clark, *Appl. Phys. Lett.*, **41**, 39 (1980).
7. N. A. Clark, M. A. Handschy and S. T. Lagerwall, *Mol. Cryst. Liq. Cryst.*, **94**, 213 (1983).
8. a) T. Sakurai, N. Mikami, R. Higuchi, M. Honma, M. Ozaki and K. Yoshino, *J. Chem. Soc. Chem. Comm.*, **978**, (1986).
   b) K. Mohr, S. Köhler, K. Worm, G. Pelzel, S. Diele, H. Zaschke, D. Demus, G. Andersson, I. Dahl, W. Kuczynsji and S. T. Lagerwall, *Mol. Cryst. Liq. Cryst.*, **146**, 151 (1987).
   c) C. Bahr and G. Heppke, *Mol. Cryst. Liq. Cryst.*, **148**, 29 (1987).
   d) H. Taniguchi, M. Ozaki, K. Yoshino, K. Satoh and N. Yamasaki *Ferroelectrics*, **77**, 137 (1988).
9. D. M. Walba, R. T. Vohra, N. A. Clark, M. A. Handschy, J. Xue, D. S. Parma, S. T. Lagerwall, and K. Skarp, *J. Am. Chem. Soc.*, **108**, 7424 (1986).
10. G. Scherowsky, J. Gay, W. Hemmerling, I. Müller, R. Wingen, H. R. Dübal, C. Escher and D. Ohlendorf, *German Pat. App.* P3718 174.2 (29.5, 1987)
11. The acceptor substituted oxirane ring has a lower basicity and therefore a higher stability against acidic ring opening.

12. H. O. House and J. W. Blaker, *J. Org. Chem.*, **80**, 6389 (1958).
13. S. T. Lagerwall, B. Otterholm and K. Skarp, *Mol. Cryst. Liq. Cryst.*, **152**, 503 (1987).
14. M. F. Bone, M. J. Bradshaw, L. K. M. Chan, D. Coates, J. Constant, P. M. Gemmel, G. W. Gray, D. Lacey and K. J. Toyne, *Mol. Cryst. Liq. Cryst.*, **164**, 117 (1988).
15. Y. Gao, R. M. Hanson, J. M. Klunder, S. Y. Ko, H. Masamune and K. B. Sharpless, *J. Am. Chem. Soc.* **109**, 5765 (1987). See also: K. B. Sharpless, T. Katsuki, *J. Am. Chem. Soc.*, **102**, 5974 (1980).
16. J. A. Dale, D. L. Dull, H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969).
17. P. H. J. Carlson, T. Katsuki, V. S. Martin and K. B. Sharpless, *J. Org. Chem.*, **46**, 3937 (1981).
18. B. Neises and W. Steglich, *Angew. Chem.*, **90**, 556 (1978).
19. H. Diamant, K. Drenck and R. Pepinsky, *Rev. Sci. Instrum.*, **28**, 30(1957).

Acknowledgment

The support by the Hoechst AG, Frankfurt and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Downloaded by [Tomsk State University of Control Systems and Radio] at 11:49 19 February 2013