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Synthesis of Some Chiral Smectics with Chloroalkoxy Side Chains†

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We have synthesized two new series of chiral esters, the (*R*)-4′-(2-chloropropoxy)phenyl 4-alkoxybenzoates (3) and the (*R*)-4′-(2-chloropropoxy)phenyl 4-alkoxycinnamates (4). Compounds belonging to the former series mainly exhibit smectic A phases at moderate temperatures (about 50°C) while the compounds of the latter series show A phases at somewhat higher temperatures. Some members of both series show, in addition, a cholesteric or a smectic B phase but tilted phases are not found at all.

Keywords: chiral smectics, phenyl benzoates, phenyl cinnamates

INTRODUCTION

With the development of the SSFLC (Surface Stabilized Ferroelectric Liquid Crystal) technique[1] synthetic efforts are now being aimed at new ferroelectric liquid crystal materials with improved properties. A good material for application according to the SSFLC-technique should have high spontaneous polarization (*P*), low viscosity, enantiotropic C* phase around room temperature and good alignment properties. The phenyl benzoates[2] (*1*) show fast ferroelectric switching,[3] in spite of moderate *P* values and thus probably have low viscosities. The presence of a smectic A phase (which facilitates alignment) made series *1* a promising candidate for further development. The analogous phenyl (*E*)-cinnamates (*2*),[4] which have thermally

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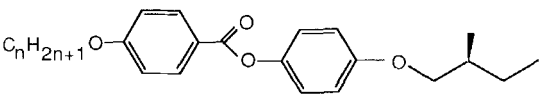
Abstract number θ-031-FE

more stable C* phases, as well as wider mesophase ranges, were also considered. Phase transition temperatures for series *1* and *2* are shown in Tables I and II, respectively.

In this paper we wish to report the replacement of the (*S*)-2-methylbutyl group of the series mentioned above by the more polar (*R*)-2-chloropropyl group (giving series *3* and *4*), the aim being to increase the spontaneous polarization.



1

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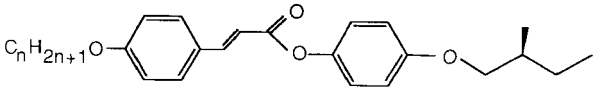

2

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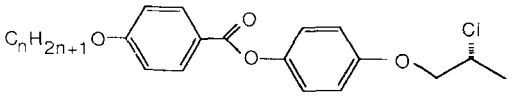
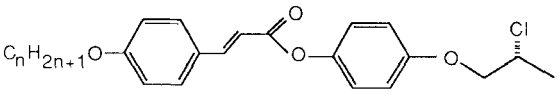


3

n=6-14



4

n=6-12, 14

TABLE I

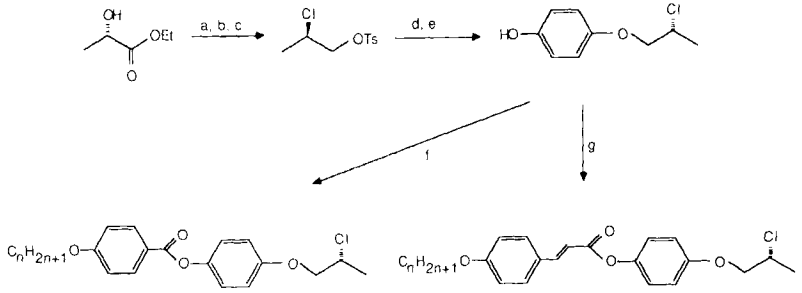
Phase transitions of series 1; X = crystal; L = isotropic liquid; N* = cholesteric; A = smectic A; C* = chiral smectic C

n	Phase transitions[a] (°C)
8	X 42 C* 43.5 A 58.5 N* 62 L
9	X 44 (C* 43.5) A 60 L
10	X 44 C* 50.2 A 65 L
11	X 49.5 (C* 48) A 63 L
12	X 49 C* 52 A 65 L

[a]From reference 2.b.

SYNTHESIS

The readily available chiral starting material for the compounds presented in this paper is (*S*)-ethyl lactate. The syntheses are carried out according to Scheme 1.



Scheme 1. a. $SOCl_2$, py; b. $LiAlH_4$, Et_2O; c. p-TsCl, py; d. *p*-Benzyloxyphenol, K_2CO_3, 2-BuOH; e. 10% Pd/C, H_2, HOAc; f. THF, Et_3N, ArCOCl; g. Et_2O, DCC, 4-pyrrolidinopyridine, ArC_2H_2COOH

(*S*)-Ethyl lactate is chlorinated with inversion[5] of configuration by tyionyl chloride/pyridine. Reduction by lithium aluminum hydride and subsequent tosylation afforded 2-chloropropyl tosylate. Displacement of the tosyl group by sodium 4-benzyloxyphenoxide furnished 1-(2-chloropropoxy)-4-benzyloxybenzene which was debenzylated to yield 4-(2-chloropropoxy)phenol. Esterification of the phenol with 4-alkoxybenzoyl chlorides or 4-alkoxycinnamic acids afforded the target esters 4′-(2-chloropropoxy)phenyl 4-alkoxybenzoates (3) and 4′-(2-chloropropoxy)phenyl 4-alkoxy cinnamates (4), respectively, in approximately 10% overall yields.

TABLE II

Phase transitions of series 2; I* = chiral smectic I; J* = chiral smectic J; for other abbreviations see Table I

n	Phase transitions[a] (°C)
6	X 98.8 (A 94.7) N* 103.4 L
7	X 89.3 (C* 84.2) A 94.6 N* 100.8 L
8	X 87.6 C* 89.5 A 101.0 N* 103.2 L
9	X 80.2 C* 92.7 A 101.7 N* 102.3 L
10	X 81.0 (I* 60.4) C* 93.9 A 103.4 L
11	X 80.0 (J* 52.2 I* 61.9) C* 94.5 A 105.1 L
12	X 79.3 (J* 50.7 I* 63.3) C* 94.9 A 103.8 L
13	X 76.3 (J* 47.3 I* 64.8) C* 94.0 A 102.8 L
14	X 74.5 (J* 45.8 I* 66.3) C* 94.4 A 102.3 L

[a]From reference 4.

RESULTS

Phase transition temperatures for compounds *3* and *4* are shown in Tables III and IV, respectively. As can be seen from Tables I and III replacement of the 2-methylbutyl group by the 2-chloropropyl group does not lead to a greater width of the mesophases; instead the C* phase vanishes and an orthogonal smectic B phase appears just before crystallisation. The melting points rise and the overall liquid crystal range narrows to about 8°C at most. The shorter homologues exhibit N* which disappears in the C_9 compound. For the C_7—C_{10} compounds a transient monotropic B phase appears just upon crystallisation. Furthermore only monotropic phases can be seen for the C_6 and C_{13}—C_{14} compounds.

The same phenomena appear in the cinnamates when the (*S*)-2-methylbutyl group is replaced by the (*R*)-2-chloropropyl group (cf.

TABLE III

Phase transitions of series 3; B = smectic B; for other abbreviations see Table I

n	Phase transitions (°C)
6	X 68.5 (N* 57) L
7	X 48 (B 31 A 47.6) N* 53.4 L
8	X 55 (B 32) A 56.4 N* 58.5 L
9	X 58 (B 33) A 61 L
10	X 61.5 (B 39) A 64.5 L
11	X 64.5 A 66 L
12	X 65.5 A 67.5 L
13	X 72 (A 68) L
14	X 73 (A 70) L

TABLE IV

Phase transitions of series 4; for abbreviations see Table III.

n	Phase transitions (°C)
6	X 107.5 (A 94.5 N* 105) L
7	X 100 (A 83 N* 91.6) L
8	X 93 (A 73.8 N* 78.7) L
9	X 100 (A 99.5) L
10	X 94 (B 69.6) A 107.5 L
11	X 92.5 A 105.5 L
12	X 95 (B 71.4) A 110 L
14	X 94.5 A 104 L

Tables II and IV). They show a narrower liquid crystal range, no C* phases and the appearance of an orthogonal B phase, evidenced as characteristic transition bars at the phase transition. These materials have only monotropic phases for C_6—C_9.

DISCUSSION

Compounds having a phenyl benzoate or similar core system are good starting structures in the search for the "ideal" ferroelectric liquid crystal. The phenyl benzoates are chemically stable, have reasonably high propensity to show C* phases and have generally low viscosity. Many of the known liquid crystal compounds of the phenyl benzoate type have the chiral 2-methylbutyl group as a tail unit. This group is rather non-polar and the dipoles contributing to the spontaneous polarization have their origin in the aromatic core system. There is therefore a weak interaction[6] between the asymmetric center and the dipole moments, resulting in a low polarization. The objective of this work was to take advantage of the good properties, especially of series *1*, and, while maintaining the low viscosity and good alignment properties, to increase the spontaneous polarization by introducing the polar chiral 2-chloropropyl unit (series 3 and 4). Recent results of, for example, Sakurai *et al.*[7] have shown that a chlorine-substituted side chain gives high spontaneous polarization. The effect in our case was, however, as can be seen above, detrimental. The smectic range decreased considerably and the C* phases vanished compared to their 2-methylbutyl analogues (cf. Tables 1, 3 and 2, 4). The reason for this is not fully understood, but as the chlorine is located at the penultimate carbon atom of the chain, the steric crowding is some-

what different from that of the methyl substituent of series 1 and 2. More examples of this situation and more comprehensive discussion of this phenomenon is given by Otterholm *et al.*[6] In some of the phenyl cinnamates which were exposed to light for several months, we found significant changes of the clearing points and the stabilities of the liquid crystalline phases. Cinnamic acids and cinnamic esters exposed to light undergo dimerization reactions (2 + 2 cycloadditions),[8] both in the solid state and in solution, and this could account for some of the deterioration of the phenylcinnamates. They probably also suffer from *E*/*Z*-isomerization.

CONCLUSION

One of the main problems in the design of ferroelectric liquid crystals is the correlation between molecular structure and smectic polymorphism. Too little is known about this to predict the liquid crystalline properties of a new material, even if only small changes are made in the molecular structure. In this work we can see that the replacement of the non-polar (*S*)-2-methylbutyl unit by the more polar (*R*)-2-chloropropyl group results in lost ferroelectric properties. One way to overcome the unfavourable branching position would be to lengthen the alkyl chain, with the chlorine atom at the same position relative the central core. This would also give a more symmetric gross molecular shape which usually increases the probability for C phases to appear. The sensitivity to light of the cinnamates makes them unsuitable for technical applications, even if used in mixtures. The more stable phenylbenzoates could, however, be a useful component in mixtures for technical applications.

EXPERIMENTAL

General

NMR spectra were recorded on a Bruker WH 270 or a Varian XL 400 instrument. High resolution mass spectra were recorded on a ZAB/HF VG analytical instrument and low resolution mass spectra on a Finnigan Mat 1020B spectrometer. IR spectra were obtained using a Perkin-Elmer 197 spectrophotometer and optical rotations using a Perkin-Elmer 241 polarimeter. Texture observations were made using an Olympus polarizing microscope in conjunction with a Mettler FP 52 hot stage and FP 5 control unit, and phase transitions were determined using a Perkin-Elmer DSC7 apparatus.

Diethyl ether, tetrahydrofuran (THF), benzene and pentane were distilled from sodium, and dichloromethane and pyridine were distilled from calcium hydride prior to use. All the target esters were purified using flash chromatography on Merck 40-63 μm normal phase silica gel with pentane/diethyl ether (9:1) or dichloromethane as eluents and recrystallized from ethanol until a clearing point interval of less than 0.5°C was obtained.

(R)-*Ethyl 2-chloropropanoate.* (*S*)-Ethyl lactate (250 g, 2.12 mol) was dissolved in pyridine (175 ml, 2.18 mol). Thionyl chloride (460 ml, 6.32 mol) was added cautiously and the mixture was stirred for 4 h at 60°C. The reaction vessel was cooled in an ice bath and cold water (300 ml) was added carefully. The mixture was extracted with ether and the ether solution washed twice with sodium hydrogen carbonate, once with dilute hydrochloric acid, once with water and once with brine. After drying over sodium sulfate the solvent was evaporated. The crude product was distilled through a Vigreux column at atmospheric pressure to yield 220 g (76%) of (*R*)-ethyl 2-chloropropanoate.

$[\alpha]_D$ +16.20°(*c* 0.636, EtOH), b.p. 142–145°C
Lit.[9] $[\alpha]_D$ +20°(neat), b.p. 143–144°C(100 kPa/760 mm Hg)
^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.38 (1H q, *J* = 6.9 Hz), 4.23 (2 H q, *J* = 7.1 Hz), 1.70 (3 H d, *J* = 6.9 Hz), 1.32 (3 H t, *J* = 7.1 Hz)

(R)-*2-Chloropropanol.* Lithium aluminum hydride (36.8 g, 0.97 mol) was suspended in dry ether (750 ml). (*R*)-Ethyl 2-chloropropanoate (220 g, 1.61 mol) dissolved in dry ether (250 ml) was added dropwise at 0°C over 2.5 h. The solution was stirred for an additional 15 h at room temperature. Water (40 ml), sodium hydroxide (40 ml, 10%) and water (120 ml) were added slowly to give insoluble aluminates. The aluminates were filtered off and washed with ether. The combined filtrate and washings were dried over magnesium sulfate and the ether was evaporated cautiously (no heating). Most of the ethanol was distilled off at atmospheric pressure to yield 116 g of crude product. A careful fractionation of the residue at reduced pressure [13 kPa (100 mm Hg)/75–78°C] was carried out to yield 53.63 g (35%) of (*R*)-2-chloropropanol.

n_D = 1.436, $[\alpha]_D$ −14.98°(*c* 8.75, CH_2Cl_2),
Lit.[10] n_D = 1.4365, b.p. 70.3–70.5°C (10 kPa/75 mm Hg)
$[\alpha]_D$ +17.39°(neat), (*S*)-2-Chloropropanol
^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.15 (1H m), 3.69 (2H m), 2.40 (1H broad), 1.50 (3H d, *J* = 6.9 Hz)

(R)-*2-Chloropropyl* p-*toluenesulfonate.* (*R*)-2-Chloropropanol (9.45 g, 0.1 mol) was dissolved in 40 ml pyridine and *p*-toluenesulfonyl chloride (19.1 g, 0.1 mol) was added in small portions at 0°C. After 1.5 h at 0°C the mixture was stirred for an additional 15 h at room temperature. The mixture was poured onto ice/hydrochloric acid and extracted with ether. The ether solution was washed three times with 2M hydrochloric acid, twice with water and once with brine. After drying (sodium sulfate) and evaporation of the solvent the product was dried in vacuum to yield 19.3 g (78%) of (*R*)-2-chloropropyl *p*-toluenesulfonate as a slightly yellow oil.

$[\alpha]_D$ −3.90° (*c* 4.433, CH_2Cl_2)
^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.80 (2 H d, *J* = 8.5 Hz), 7.36 (2 H d, *J* = 8.5 Hz), 4.0–4.2 (3 H m), 2.46 (3 H s), 1.50 (3 H d, *J* = 6.9 Hz)

(R)-*1-(2-Chloropropoxy)-4-benzyloxybenzene.* (*R*)-2-Chloropropyl *p*-toluenesulfonate (19.3 g, 77.7 mmol) and *p*-benzyloxyphenol (16.0 g, 80 mmol) were refluxed with potassium carbonate (22.1 g, 160 mmol) in 2-butanol (120 ml) for 18 h. The mixture was cooled, diluted with 100 ml water and then extracted twice with ether. The combined organic layers were washed twice with 10% sodium hydroxide, twice with water, dried over sodium sulfate and the solvent evaporated. The residue was chromatographed on silica gel (70–200 mesh, dichloromethane) to yield 19.2 g (90%) of (*R*)-1-(2-chloropropoxy)-4-benzyloxybenzene as colourless crystals.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.38 (5 H m), 6.87 (4 H m), 5.02 (2 H s), 4.18 (1 H m), 4.09 (1 H dd, J_{gem} = 10 Hz, J_{vic} = 6 Hz), 3.96 (1 H dd, J_{gem} = 10 Hz, J_{vic} = 6 Hz), 1.60 (3 H d, *J* = 6.9 Hz)

(R)-*4-(2-Chloropropoxy)phenol.* A 100 ml round-bottomed flask charged with acetic acid (40 ml) and Pd/C (0.3 g, 10% Pd) was evacuated and filled with argon, then evacuated again and filled with hydrogen and finally a balloon filled with hydrogen was connected. (*R*)-1-(2-Chloropropoxy)-4-benzyloxybenzene (4.54 g, 15 mmol) was added and the mixture was stirred vigorously for about 4 h. The Pd/C was filtered off and the solvent evaporated. The product was chromatographed on silica gel (70–200 mesh, dichloromethane) to yield 2.5 g (95%) of (*R*)-4-(2-chloropropoxy)phenol as a colourless oil.

$[\alpha]_D$ −14.05° (*c* 2.377, CH_2Cl_2)
^{1}H NMR (270 MHz, $CDCl_3$): δ = 6.76 (4 H m), 4.25 (1 H m), 4.08 (1 H dd, J_{gem} = 10 Hz, J_{vic} = 6 Hz), 3.95 (1 H dd, J_{gem} = 10 Hz, J_{vic} = 6 Hz), 1.58 (3 H d, J = 6.3 Hz)
IR (CH_2Cl_2): 3575, 2920, 2860, 1505, 1225, 1175, 1020, 825 cm^{-1}
HRMS: Mol. wt., obs. 186.043, calc. for $C_9H_{11}ClO_2$ 186.045
MS (70 eV, m/Z): 188 (M^+ +2, 14%), 186 (M^+, 31%), 112 (100%), 82 (60%), 65 (36%)

4-Alkoxybenzoic acids were prepared by a standard procedure[11] from 4-hydroxybenzoic acid, and their transitions were in accord with the literature.[12]

Representative procedure for preparing 4-alkoxybenzoyl chlorides.

4-Decyloxybenzoyl chloride. 4-Decyloxybenzoic acid (3.29 g, 11.8 mmol) was dissolved in benzene (40 ml). Oxalyl chloride (2.1 ml, 24.4 mmol) was added and the solution was stirred at room temperature and under argon for 15 h. The benzene was evaporated and the crude product was distilled using a Kugelrohr apparatus [6 Pa (0.06 mbar)/110°C] to yield 3.34 g (95.5%) of 4-decyloxybenzoyl chloride.

M.p. <23°C
^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.07 (2 H d, J = 8.8 Hz), 6.95 (2 H d, J = 8.8 Hz), 4.04 (2 H t, J = 6.6 Hz), 1.82 (2 H m), 1.22–1.50 (14 H m), 0.89 (3 H t, J = 6.8 Hz)
MS (70 eV, m/Z): 298 (M^+ +2, 0.6%), 296 (M^+, 1.6%), 261 (28%), 122 (86%), 92 (15%), 56 (100%)

Representative procedure for coupling of (*R*)-4-(2-chloropropoxy)phenol with 4-alkoxybenzoyl chlorides.

(R)-*4'-(2-Chloropropoxy)phenyl 4-decyloxybenzoate.* 4-Decyloxybenzoyl chloride (470 mg, 1.6 mmol) was dissolved in THF (3 ml) under argon at room temperature. (*R*)-4-(2-Chloropropoxy)-phenol (300 mg, 1.6 mmol) in THF (3 ml) and triethylamine (0.29 ml, 2.1 mmol) were added and the resultant mixture was stirred for 2.5 h. Water was added and the mixture was extracted with ether. The ethereal solution was washed twice with 2M hydrochloric acid, and then with water, dilute sodium hydrogencarbonate and brine. The

solution was dried over sodium sulfate, the solvent evaporated and the crystalline product was chromatographed on silica gel (pentane/ether 9:1) and recrystallized twice from ethanol to yield 480 mg (68%) of 4′-(2-chloropropoxy)phenyl 4-decyloxybenzoate.

$[\alpha]_D$ −4.00 (*c* 1.624, CH_2Cl_2)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (2 H d, *J* = 8.8 Hz), 7.12 (2 H d, *J* = 8.8 Hz), 6.96 (4 H m), 4.30 (1 H m), 4.13 (1 H dd, J_{gem} = 10 Hz, J_{vic} = 6 Hz), 4.04 (3 H m), 1.81 (2 H m), 1.63 (3 H d, *J* = 6.8 Hz), 1.20–1.52 (14 H m), 0.89 (3 H t, *J* = 6.8 Hz)
IR (CH_2Cl_2): 2920, 2850, 1720, 1600, 1500, 1190, 1165, 1070 cm^{-1}
HRMS: Mol. wt., obs. 446.224, calc. for $C_{26}H_{35}ClO_4$ 446.223
MS (70 eV, *m/Z*): 448 (M^+ + 2, 0.3%), 446 (M^+, 0.8%), 262 (60%), 122 (100%), 109 (15%), 93 (26%), 65 (17%), 55 (19%)

Homologues esters of this series (*3*) gave ^{1}H NMR, IR, HRMS and MS data entirely consistent with the required structures and purities for the materials. These data are available on application to the authors.

4-Alkoxycinnamic acids. The procedure[11] for alkylating 4-hydroxybenzoic acid was applied to 4-hydroxycinnamic acid, and the products had transitions in accord with the literature.[12]

Representative procedure for coupling of (*R*)-4-(2-chloropropyloxy)phenol with 4-alkoxycinnamic acids.

(R)-*4′-(2-Chloropropoxy)phenyl 4-decyloxycinnamate.* 4-Decyloxycinnamic acid (1.01 g, 3.33 mmol), (*R*)-4-(2-chloropropoxy)phenol (0.6 g, 3.33 mmol) and dicyclohexylcarbodiimide (0.66 g, 3.33 mmol) were added to dry ether (15 ml). 4-Pyrrolidinopyridine (0.05 g, 0.33 mmol) was added and the mixture was stirred at room temperature overnight. The urea was filtered off and the filtrate was washed three times with water, three times with 5% acetic acid and three times with water. Finally, the ethereal phase was dried over sodium sulfate, the solvent evaporated and the residue chromatographed on silica gel with dichloromethane as eluent. The product was recrystallized from ethanol to yield 0.4 g (26%) of (R)-4′-(2-chloropropoxy)phenyl 4-decyloxycinnamate as white crystals.

$[\alpha]_D$ −1.04° (*c* 2.115, CH_2Cl_2)
^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.81 (1 H d, *J* = 15.7 Hz), 7.52

(2 H d, J = 8.8 Hz), 7.09 (2 H d, J = 8.8 Hz), 6.93 (4 H m), 6.48 (1 H d, J = 15.7 Hz), 4.28 (1 H m), 4.11 (2 H m), 3.98 (2 H m), 1.80 (2 H m), 1.62 (3 H t, J = 7.2 Hz), 1.22–1.50 (14 H m), 0.89 (3 H t, J = 7.2 Hz)
IR (CH_2Cl_2): 2920, 2850, 1715, 1625, 1600, 1500, 1195, 1170, 1130, 825 cm^{-1}
HRMS: Mol. wt., obs. 472.237, calc. for $C_{28}H_{37}ClO_4$ 472.238
MS (70 eV, m/Z: 474 (M^+ +2, 0.1%), 472 (M^+, 0.3%), 287 (74%), 147 (100%), 119 (40%), 91 (21%), 55 (21%)

Homologues esters of this series (4) gave ^1H NMR, IR, HRMS and MS data entirely consistent with the required structures and purities for the materials. These data are available on application to the authors.

Acknowledgments

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