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K. Fodor-csorba [a], A. Vajda [a], L. Bata [a], S. Holly [b], E. Gács-Baitź [b], K. Újszászy [c], J. C. Lee [d] & Y. J. Jeon [d]

[a] Research Institute for Solid State Physics of the Hungarian Academy of Sciences, P.O. Box 49, H-1525, Budapest, Hungary

[b] Central Research Institute for Chemistry of the Hungarian Academy of Sciences, P.O. Box 17, H-1525, Budapest, Hungary

[c] EGIS Pharmaceutical CO., P.O. Box 100, H-1475, Budapest, Hungary

[d] SAMSUNG Advanced Institute of Technology, Display Laboratory, P.O. Box 111, Suwon, Korea, 440-600

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SYNTHESIS OF LIQUID CRYSTALS CONTAINING CHLORINE ON THE CHIRAL CENTER

K. FODOR-CSORBA, A. VAJDA, L. BATA

Research Institute for Solid State Physics of the Hungarian Academy of Sciences H-1525 Budapest, P.O.Box 49. Hungary,

S. HOLLY, E. GÁCS-BAITZ

Central Research Institute for Chemistry of the Hungarian Academy of Sciences H-1525 Budapest, P.O.Box 17, Hungary

K. ÚJSZÁSZY

EGIS Pharmaceutical CO., H-1475 Budapest, P.O.Box 100, Hungary

J.C. LEE, Y.J. JEON

SAMSUNG Advanced Institute of Technology, Display Laboratory, P.O. Box 111, Suwon, Korea 440-600

Abstract

A synthetic pathway is described for the preparation of the homologous series of (R)-(2-chloropropyl)-4-[4'-(n-alkoxy)benzoyl-oxy] benzoates with high optical purity. The liquid crystalline members of the series exhibit smectic A^* phase and can be used as chiral dopants in ferroelectric mixtures. The n=8 member was used in a mixture exhibiting monotropic and the n=9 member enantiotropic smectic C^* phase around room temperature.

Introduction

The liquid crystals containing large dipole moment around the chiral center are useful in ferroelectric mixtures exhibiting large spontaneous polarization values and short response time. Some representatives such compounds have been synthesized from α-halogen carboxylic acid derivatives[1-3]. Several liquid crystalline derivatives of lactic acid were described where chlorine or alkyl ethers are connected to the chiral center. The 4'-(ω-(2-ethoxy)propoxy)

alkoxyphenyl 4-alkoxybenzoates exhibited enantiotropic smectic C^* phase, the other series showed mainly S_A and S_B phases[4]. 4'-[(R)-(2-chloropropoxy)]phenyl-4-alkoxybenzoates and 4'-[(R)-(2-chloropropoxy)]phenyl-4-alkoxy-cinnamate homologous series were also published exhibiting smectic A phase at moderate temperatures. Some members of this series showed cholesteric and smectic B^* phases, but tilted phases were not found[5]. Some stable lactic ether and chiral epoxy compounds were also published exhibiting smectic A^* and monotropic smectic C^* phase with fairly high spontaneous polarization[6,7]. (R)-(2-chloropropyl) and (R)-(2-chloropropyl)phenyl-4-[4'-(n-alkoxy)-biphenyl]carboxylates were synthesized[8] too.

This paper describes the preparation of (R)-(2-chloropropyl)-4-[4'-(n-alkoxy)benzoyloxy]benzoates (**1a-i**) (see Figure 2.). Although this homologous series (n=1-14) was claimed[9], one can find the phase transition data only for the n=10 member. The other members of this series were only claimed but neither the optical rotation and spectroscopic data, nor the phase transition temperatures have been given. We have synthesized the n=4,5,7-12,16 (**1a-i**) members of this homologous series having a chlorine atom connected to the chiral center. These compounds exhibit smectic A phase serving as chiral dopants in ferroelectric mixtures.

A new synthetic procedure is described here leading to the series of **1a-i**. All the members of the homologous series and their intermediates were checked by infrared (IR), nuclear magnetic resonance (^{1}H NMR) and mass spectroscopy (MS). The optical activity of the compounds was also established.

RESULTS AND DISCUSSION

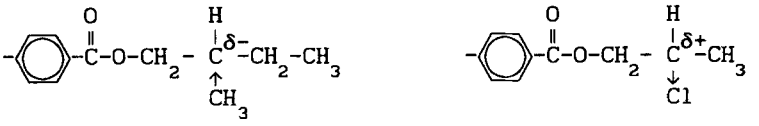
(R)-(2-chloropropyl)-4-[4'-(n-alkoxy)benzoyloxy] benzoates (**1a-i**) were prepared in high optical purity. Here we have used a protecting group for avoiding the racemization during the synthetic process.

The methoxycarbonyloxy group was suggested to protect the phenolic OH group earlier[12]. The ethoxycarbonyloxy group could be used with just as good efficiency in our experiments. Both of these protecting groups are resistant in acidic conditions but can be easily decoupled in alkaline media.

The 4-hydroxybenzoic acid can be reacted with (S)-2-methylbutyl

alcohol using acid catalysis (e.g. p-toluenesulphonic acid or cc. H_2SO_4, etc.) in the condensation reaction, the optical purity of the ester is high enough. On the contrary, the reaction between 4-hydroxy-benzoic acid and (R)-2-chloro-1-propanol led to considerable racemization during this direct ester formation.

The esters of 2-methylbutyl and 2-chloropropyl alcohols are shown in Figure 1.



12 **13**

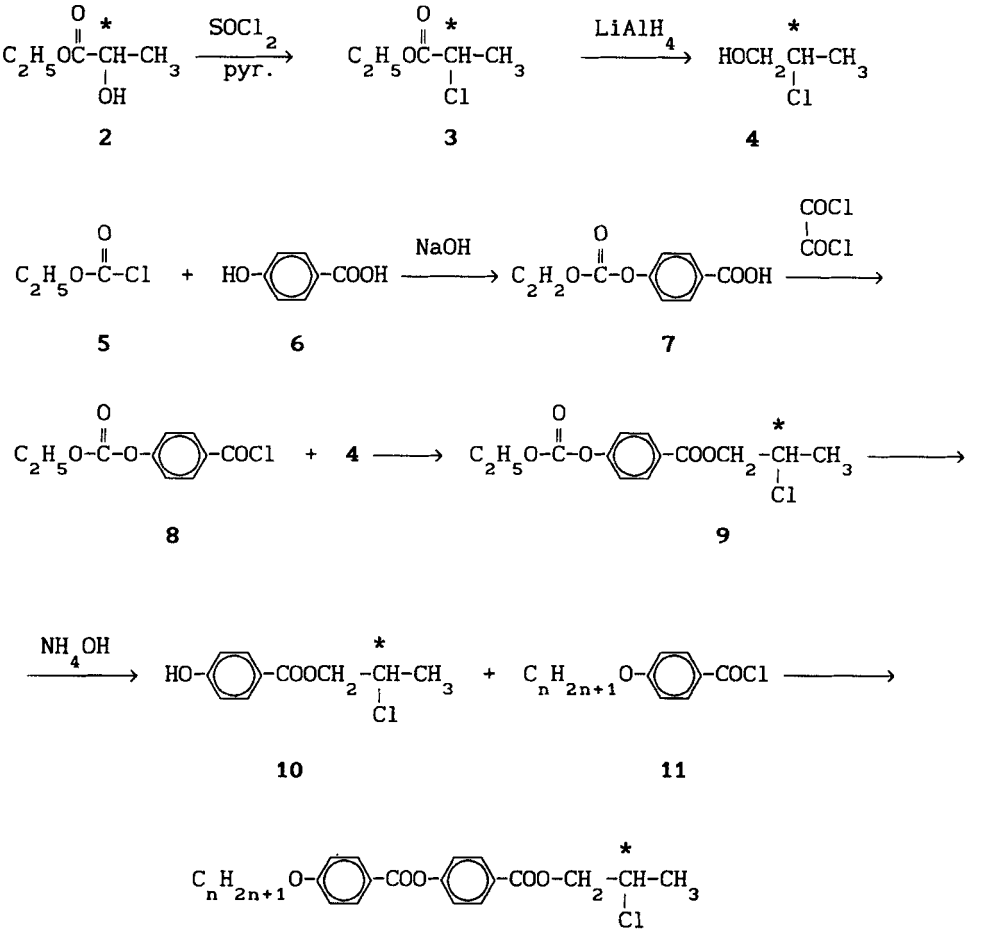
FIGURE 1. Inductive effects around the chiral centers

The methyl group with its positive inductive effect enhances the electron density around the chiral center, this center can be considered slightly negatively charged (δ-) in compound **12** (Figure 1). The opposite can be seen in case of the 2-chloropropyl ester **13** (Figure 1). The strong electron withdrawing effect of the chlorine (electronegativity of 3 on the Pauling scale) causes a lower electron density (δ+) around the chiral center, further on the C-H bond of the chiral center became rather loosened. This effect causes racemization in the latter case during the acid catalyzed ester formation.

This phenomenon makes understandable the usage of a protecting group in the synthetic process opening a pathway carried out in mild conditions.

There was another possibility instead of the direct esterification, e.g. the usage of dicyclohexyl carbodiimide in the presence of dimethylaminopyridine used as a catalyst. Though the protection of the phenolic OH group was also necessary, the compounds obtained were difficult to clean from the byproduct, i.e. dicyclohexyl urea.

The homologous series was prepared according to the reaction scheme in Figure 2.



1a-i

FIGURE 2. Reaction scheme for the preparation of (R)-(2-chloropropyl)-4-[4'-(n-alkoxy)benzoyloxy] benzoates

The detailed IR spectroscopic characterization of these compounds is given in the experimental part. The characteristic frequencies are given for aliphatic CH, aromatic ring and carbonyl groups. The exact frequencies of the overlapped ester carbonyl bands were determined by the help of the second derivative spectra between 1800 and 1650cm^{-1} (see Figure 3 for **1e** (n=9 member)).

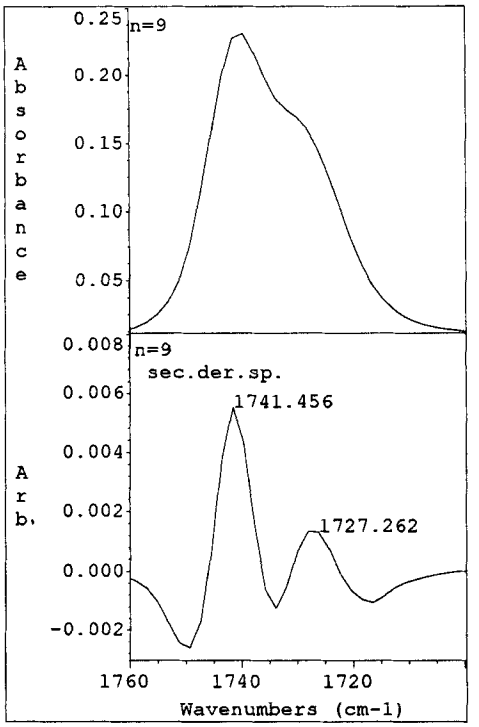


FIGURE 3. IR and second derivative spectrum of the ester carbonyl bands of **1e** (n=9 member).

The assignations of the ^1H NMR signals are listed in the experimental part; the numbering of the protons is indicated in Figure 4.

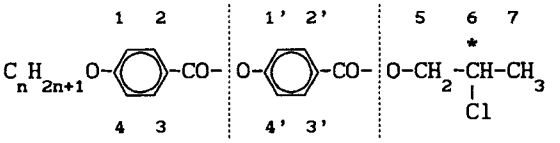


Figure 4. Numbering of the protons for ^1H NMR assignation and the main fragmentation routes of **1a-i** in mass spectra.

The main fragmentation routes observable in the mass spectra are shown in Figure 4 as dotted lines.

Phase transitions of the series are summarized in Table I.

TABLE I Properties of the homologous series.

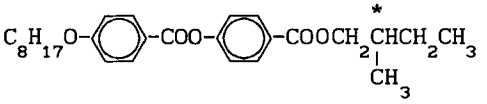
Compounds	Phase Transition Temperatures in °C				
	C	·	S_A^*	·	I
1a (n=4)	·	91	-	-	·
1b (n=5)	·	90	-	-	·
1c (n=7)	·	68	(·	67)	·
1d (n=8)	·	52	·	68	·
1e (n=9)	·	52	·	69	·
1f (n=10)	·	63	·	69	·
1g (n=11)	·	61.5	·	74.5	·
1h (n=12)	·	56	·	75	·
1i (n=16)	·	52	·	65	·

( ) monotropic transition

The lower homologoues (**1a**, **1b**) have no liquid crystalline phases. The **1c** has monotropic and the higher homologoues (**1d-i**), exhibit enantiotropic S_A phases. None of the compounds synthetized here exhibited S_C^* phase. However, these materials with the perpendicular dipole, i.e. the chlorine connected to the chiral center might cause high spontaneous polarization in ferroelectric mixtures. The lack of S_C^* phase may be the consequence of the space filling of the chlorine atom on the chiral center, and the resulting large width/length ratio of the chiral group.

Our aim was to prepare some multicomponent ferroelectric mixtures having a broad range of S_C^* phase under S_A^* phase. It is well known from the literature[14] and from our investigations that mesogens having no S_C^* phase and chiral non-mesogenic compounds can be useful as mixture components.

We have checked **1d** as a chiral dopant in a binary mixture. (S)-(2-methylbutyl)-4-[4'-(n-octyloxy)benzoyloxy] benzoate (**14**) was



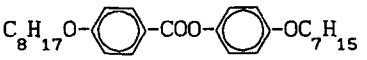
Cr (31 S_C^*) 34 S_A^* 57 I

14

chosen as a main component which exhibits monotropic S_C^* phase in the

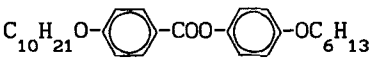
temperature range 18-31°C. The dopant **1d** was applied in concentration of 5%. Although the dopant has only S_A^* phase, the short monotropic S_C^* phase of the basic component was preserved, only its range got narrower by five degrees. Phase transition temperatures of this binary mixture (mixture **I**) are shown in Table II.

Since mixture **I** exhibited only a monotropic S_C^* phase (20-28°C), we studied other mixtures to obtain enantiotropic S_C^* phase around room temperature. Mixture **II** was the eutectic mixture of (4'-n-heptyloxyphenyl)-4-n-octyloxy benzoate (**15**) and (4'-n-hexyloxyphenyl)-4-n-decyloxy benzoate (**16**) having a broad (40°C) enantiotropic S_C phase (Table II). Mixture **II** was used as a non-chiral host mixture.



Cr 62 Sc 69 N 88 I

15



Cr (45 S_B) 77 S_A 83 N 89 I

16

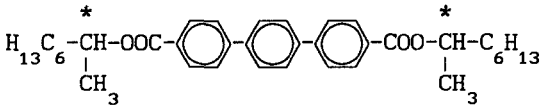
Some chiral dopants were applied in order to get higher spontaneous polarization of the mixtures. Compound **14** was the basic component of mixture **I** but it was applied as a chiral additive in mixture **III**.

TABLE II. Phase sequences of the multicomponent mixtures.

Number of mixtures	Basic mixtures (w%)		Dopant compound (w%)		Phase sequence and transition temperatures (C°)
I	**14**	95.0	**1d**	5.0	Cr(28 S_C^*) 33 S_A^* 57 I
II	**15**	55.0	-	-	Cr(33 S_B) 43 S_C 73 S_A 78 N 88 I
	16	45.0			
III	**15**	45.8	**14**	16.7	Cr(31 S_B^*) 39 S_C^* 42 S_A^* 80 N^* 83 I
	16	37.5			
IV	**15**	47.8	**14**	8.7	Cr(31 S_B^*) 39 S_C^* 43 S_A^* 81 N^* 85 I
	16	39.1	**1e**	4.4	
V	**15**	38.5	**17**	15.4	Cr 40 S_C^* 67 S_A^* 81 I
	16	38.5	**1e**	7.7	

Mixture **III** has an enatiotropic S_C^* phase near room temperature. Its S_A^* phase temperature range has broadened from 5°C to 38°C offering an appropriate mixture for electroclinic measurements. Decreasing the concentration of **14** in mixture **IV** and using the chlorine containing **1e** as chiral dopant, no considerable changes in the phase transition temperatures were observed in mixtures **III** and **IV** (Table II). The S_C^* phases of the mixtures **II, III, IV** can be supercooled to temperatures well below the melting points.

Since compound **14** caused a dramatic narrowing of the S_C^* phase in the mixtures applied, it was advisable to replace this compound. Though bis(S)-(1-methylheptyl)-1,1'-4',1''-terphenyl-1,4''-dicarboxylate[13]



17

(**17**) is a non-mesogenic compound, it has a stabilizing effect on the S_C^* phase. Using compound **17** in larger quantity instead of compound **14** in mixture **V**, the S_C^* phase became as broad as the S_C phase of the original host mixture **II** (Table II).

Mixtures **III, IV, V** are examples of substances showing induced ferroelectricity since they are composed of non-chiral hosts and appropriate chiral additives.

EXPERIMENTAL

Confirmation of the structure of intermediates and products was obtained by the following methods:

Infrared spectra (IR) were taken with a NICOLET 170SX and NICOLET MAGNA 750 FT-IR spectrometers in CCl_4, or $CHCl_3$ solutions. The concentration of the samples was uniformly 1mg/1ml solvent; thickness of KBr cell was 0.086mm, resolution was $4cm^{-1}$.

^1H NMR spectra were recorded on a VARIAN XL-400 spectrometer at 25°C, the chemical shifts (δ) are referred to internal tetramethylsilane. ^1H assignments, if necessary, were performed with the aid of homonuclear spin decoupling experiments.

Mass spectra were taken with a KRATOS MS-25-RFA instrument with the following settings: ion accelerating voltage 70eV, trap current 100μA, direct introduction, 200°C.

The phase transition temperatures were obtained by means of microscopical observations of the textures with a PHMK 80/2914 polarizing microscope equipped with a Boetius hot stage.

The optical rotation data were measured with a POLAMAT A polarimeter, solvents and concentrations are given at the compounds concerning.

Thin-layer chromatography was used to follow the reaction procedures and for checking the purity of the compounds. The Rf values are given at the compounds.

R(+) Ethyl 2-chloropropionate (**3**)[10]: Half portion of the thionyl chloride (36g, 0.25mol) under N_2 stream was added slowly to the stirred and slightly cooled (S)-ethyl-lactate (**2**) (60g, 0.5mol, $[\alpha]_D^{20}$= -10.8 neat [Merck]). After two hours stirring the second portion of the thionyl chloride (36g, 0.25mol) was added and the reaction mixture was left to stand overnight. Several drops of pyridine were added to the reaction mixture which was heated for four hours in a bath maintained at 100°C. After distillation at 44°C/2 kPa **3** was obtained: 51-54g, 75-80% yield, $[\alpha]_D^{20}$= +20.0, neat l=1dm.

R(-)-2-chloro-1-propanol (**4**)[11]:Lithium aluminium hydride (4.85g, 127mmol) was stirred in 130ml dry ether and **3** (23.0g, 168.5mmol) was given with the speed keeping the solvent slightly boiling during the addition. After two hours stirring 20ml saturated water solution of magnesium sulfate was added to the mixture and the salts formed were filtered off. The ether solution was dried over magnesium sulfate, the solvent evaporated and **4** distilled: 12.41g, 78% yield, bp: 53°C/3.4kPa, $[\alpha]_D^{22.6}$=20.6, neat l=1dm.

4-Ethoxycarbonyloxybenzoic acid (**7**): Sodium hydroxide (30g 0.75mol) was dissolved in 800ml water and at +5°C 4-hydroxybenzoic acid (35.8g, 0.26mol) was added. Later ethyl chloroformate (43.4g, 0.4mol) was introduced dropwise to the well stirred reaction mixture when the temperature was maintained at +5°C. After finishing the addition the reaction mixture was stirred for four hours. The pH 5 was adjusted by 20% (v/v) HCl solution and the precipitate formed was filtered off, dried and recrystallized from benzene: 49.1g, ~90% yield, mp:156-7°C.

4-Ethoxycarbonyloxybenzoyl chloride (**8**): Oxalyl chloride was added slowly to **7** (7g, 33.3mmol) and the resulting solution was heated under reflux for four hours. The excess of the oxalyl chloride was removed by distillation under reduced pressure and the remaining **8** was used without further purification: 7.2g.

(R)-(2-chloropropyl)-4-ethoxycarbonyloxybenzoate (**9**): Potassium carbonate (24.8g, 180mmol) and **8** (25.5g, 120mmol) were added to the stirred ether solution (300ml) of **4** (11.3g, 120mmol). The reaction mixture was refluxed for 5 hours. After cooling and filtrating, the solvent was evaporated and the product was purified either by crystallization or by flash chromatography on Kieselgel 60 (Merck) column eluted with ethyl acetate. Finally fractions containing Rf: 0.66 spot were collected and recrystallized in ethyl or methyl alcohol: 25g, 72.7% yield.

(R)-(2-chloropropyl)-4-hydroxybenzoate (**10**): (R)-(2-chloropropyl--4-(ethoxycarbonyloxy) benzoate (15g, 52.3mmol) was dissolved in 100ml ethyl alcohol and ammonium hydroxide (110ml 25% (w/v)) was dropped to it at +5°C. After 10 minutes stirring the pH 5 was adjusted with 5% HCl solution. The cold reaction mixture was extracted with 200ml cold ethyl acetate. The organic layer was quickly washed with brine dried over magnesium sulfphate and the solvent was evaporated. The crude product was recrystallized from ethyl alcohol and finally from benzene: 7.8g, 70% yield, Rf:0.32 in n-hexane:ethyl acetate 2:1 system, $C_{10}H_{11}ClO_3$ M=214.5, mp:124-5°C, $[\alpha]_D^{20}$=-14.64 (c=3.11 ethanol), IR ($CHCl_3$): 3587 νOH, 2984 $\nu_{as}CH_3$, 2955 $\nu_{as}CH_2$, 1712 νC=O, 1609 $\nu C_{Ar}C_{Ar}$, 1272 ν_{as}C-O-C cm^{-1}; ^{1}H NMR $CDCl_3$, δ(ppm): 1.62(d,3H, J=6.5Hz, H7), 4.31(m,1H,H6), 4.41(d,2H, J=6Hz, H5), 6.45(bs,1H,OH), 6.9(d,2H,H1+H4), 7.99(d,2H, H2+H3).

General procedure for preparation of the homologous series of (R)-(2-chloropropyl)-4-[4'-(n-alkoxy)benzoyloxy] benzoates (**1a-i**): The 4-n-alkoxybenzoyl chloride (1mol) in absolute benzene solution was given to the stirred absolute benzene solution of **10** (1mol) in the presence of pyridine (1mol). The reaction mixture was stirred overnight, poured on water. After separation, the organic layer was extracted several times with 3% HCl solution, water, 3% sodium bicarbonate solution and water, dried over magnesium sulphate and the solvent was evaporated. The residue was recrystallized from ethanol,

methanol several times. The purity of the compounds was checked by thin-layer chromatography on Kieselgel 60 F_{254} plates eluted with n-hexane:ethyl acetate 2:1 system. The Rf values are given at the individual compounds.

1a: n=4, $C_{21}H_{23}ClO_5$, Rf:0.53, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1742, 1727 $\nu C{=}O$, 1605, 1581, 1511, $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ(ppm): 0.98 (t,3H,CH_3), 1.60(d,3H, J=6.5Hz, H7), 1.48-1.85(m,4H, 2x aliphatic CH_2), 4.06(t,2H, J=6.5Hz, OCH_2), 4.33(m,1H, H6), 4.44(d,2H, J=6Hz, H5), 6.95(d,2H,H1+H4), 7.32(d,2H,H1'+H4'), 8.15(d,4H,H2+H3+H2'+H3'), MS: m/z 390(M^+, 0.2%), 297(2%), 177(50%), 121(100%), $[\alpha]_D^{20}$=-18.40 (c=10 benzene).

1b: n=5, $C_{22}H_{25}ClO_5$, Rf:0.55, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1742, 1727 $\nu C{=}O$, 1605, 1581, 1511 $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ(ppm): 0.94(t,3H, CH_3), 1.60(d,3H, J=6.5Hz, H7), 1.35-1.85(m,6H, 3x aliphatic CH_2), 4.06(t,2H, J=6.5Hz, OCH_2), 4.33(m,1H,H6), 4.44(d,2H, J=6Hz, H5), 6.95(d,2H,H1+H4), 7.31(d,2H,H1'+H4'), 8.14(d,4H,H2+H3+H2'+H3'), MS: m/z 404(M^+, 0.2%), 311(2%), 191(50%), 121(100%), $[\alpha]_D^{20}$=-17.05 (c=10 benzene).

1c: n=7, $C_{24}H_{29}ClO_5$, Rf:0.56, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1744, 1732 $\nu C{=}O$, 1605, 1581, 1511 $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ(ppm): 0.90(t,3H, CH_3), 1.25-1.85(m,10H, 5x aliphatic CH_2), 1.62(d,3H, J=6.5Hz, H7), 4.05(t,2H, J=6.5Hz, OCH_2), 4.33(m,1H,H6), 4.44(d,2H, J=6Hz, H5), 6.96(d,2H,H1+H4), 7.32(d,2H,H1'+H4'), 8.13(d,4H,H2+H3+H2'+H3'), MS: m/z 432(M^+, 0.2%), 339(2%), 219(50%), 121(100%), $[\alpha]_D^{20}$=-16,20 (c=10 benzene).

1d: n=8, $C_{25}H_{31}ClO_5$, Rf:0.58, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1741, 1727 $\nu C{=}O$, 1605, 1581, 1511 $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ(ppm): 0.9(t,3H, CH_3), 1.25-1.85(m,12H, 6x aliphatic CH_2), 1.59(d,3H, J=6.5Hz, H7), 4.06(t,2H, J=6.5Hz, OCH_2), 4.32(m,1H,H6), 4.45(d,1H, J=6Hz, H5), 6.97(d,2H,H1+H4), 7.31(d,2H,H1'+H4'), 8.12(d,4H, H2+H3+H2'+H3'), MS: m/z 446(M^+, 0.2%), 353(2%), 233(50%), 121(100%), $[\alpha]_D^{20}$=-10.27 (c=10 benzene).

1e: n=9, $C_{26}H_{33}ClO_5$, Rf:0.58, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1741, 1727 $\nu C{=}O$, 1605, 1581, 1511 $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ(ppm): 0.88(t,3H, CH_3), 1.25-1.85(m,14H 7x aliphatic CH_2), 1.59(d,3H, J=6.5Hz, H7), 4.04(t,2H, J=6.5Hz, OCH_2), 4.32(m,1H,H6), 4.43(d,2H, J=6Hz, H5), 6.98(d,2H,H1+H4), 7.31(d,2H,H1'+H4'), 8.12(d,4H, H2+H3+H2'+H3'), MS:

m/z 460(M^+ 0.2%), 367(2%), 247(50%), 121(100%), $[\alpha]_D^{20}$=-16.70 (c=10 benzene).

1f: n=10, $C_{27}H_{35}ClO_5$, Rf:0.59, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1741, 1728 $\nu C{=}O$, 1605, 1581, 1511 $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ(ppm): 0.89(t,3H, CH_3), 1.25-1.85(m,16H, 8x aliphatic CH_2), 1.61(d,3H, J=6.5Hz, H7), 4.04(t,2H, J=6.5Hz, OCH_2), 4.33(m,1H,H6), 4.43(d,2H, J=6Hz, H5), 6.98(d,2H,H1+H4), 7.30(d,2H,H1'+H4'), 8.11(d,4H,H2+H3+H2'+H3'), MS: m/z 474(M^+, 0.2%), 381(2%), 261(50%), 121(100%), $[\alpha]_D^{20}$=-16.50 (c=10 benzene).

1g: n=11, $C_{28}H_{37}ClO_5$, Rf:0.61, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1741, 1727 $\nu C{=}O$, 1605, 1581, 1511 $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ (ppm): 0.89 (t, 3H, CH_3), 1.25-1.85 (m, 18H, 9x aliphatic CH_2), 1.60 (d, 3H, J=6.5Hz, H7), 4.05 (t, 2H, J=6.5Hz, OCH_2), 4.32 (m, 1H, H6), 4.44 (d, 1H, J=6Hz, H5), 6.98 (d, 2H,H1+H4), 7.32 (d, 2H, H1'+H4'), 8.12 (d, 4H, H2+H3+H2'+H3'), MS: m/z 488 (0.2%), 395 (2%), 275 (50%), 121 (100%), $[\alpha]_D^{20}$=-11.50 (c=5 benzene)

1h: n=12, $C_{29}H_{39}ClO_5$, Rf:0.62, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1741, 1722 $\nu C{=}O$, 1605, 1581, 1511 $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ(ppm): 0.89(t,3H,CH_3), 1.25-1.85(m,20H, 10x aliphatic CH_2), 1.61(d,3H, J=6.5Hz, H7), 4.05(t,2H, J=6.5Hz, OCH_2), 4.32(m,1H, H6), 4.44(d,1H, J=6Hz, H5), 6.97(d,2H,H1+H4), 7.32(d,2H,H1'+H4'), 8.11(d,4H,H2+H3 +H2'+H3'), MS: m/z 502(0.2%), 409(2%), 289(50%), 121(100%), $[\alpha]_D^{20}$=-7.35 (c=4 benzene).

1i: n=16, $C_{33}H_{47}ClO_5$, Rf:0.62, IR (CCl_4): 2990-2800 $\nu C_{Al}H$, 1741, 1722 $\nu C{=}O$, 1605, 1581, 1511 $\nu C_{Ar}C_{Ar}cm^{-1}$, ^1H NMR $CDCl_3$, δ(ppm): 0.89(t,3H, CH_3), 1.24-1.85(m,28H, 14x aliphatic CH_2), 1.62(d,3H, J=6.5Hz, H7), 4.06(t,2H, J=6.5Hz, OCH_2), 4.33(m,1H, H6), 4.44(d,2H, J=6Hz, H5), 6.98(d,2H,H1+H4), 7.31(d,2H,H1'+H4'), 8.12(d,4H,H2+H3+H2'+H3'), MS: m/z 558(0.2%), 465(2%), 345(50%), 121(100%), $[\alpha]_D^{20}$=-6.77 (c=2.98 benzene).

Conclusions

A homologous series of (R)-(2-chloropropyl)-4-[4'-(n-alkoxy) benzoyloxy] benzoates (**1a-i**) was prepared. In the synthesis ethoxycarbonyloxy protecting group was used to avoid the racemization observed in the direct esterification. The members of the series exhibited smectic A^* phases and were useful as chiral additives in ferroelectric mixtures. This property of compounds was exploited in

some multicomponent mixtures having S_C^* phase around room temperature. The electroclinic effect and the spontaneous polarization of these substances are studied currently.

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