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Ferroelectric liquid crystals containing a 2(*S*)-[2(*S*)-methylbutoxy]propionyloxy unit

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A new chiral organic acid, 2(*S*)-[2(*S*)-methylbutoxy]propionic acid (**2**), was synthesized from ethyl lactate and (*S*)-1-iodo-2-methylbutane. The acid **2** containing two centres of chirality was used as a building block for preparing ferroelectric liquid crystals. Three series of chiral compounds were synthesized to study the influence of the molecular structures on the formation of liquid crystal phases. They are 4-{2(*S*)-[2(*S*)-methylbutoxy]propionyloxy}phenyl 4-*n*-alkoxybenzoate (series A), 4-{2(*S*)-[2(*S*)-methylbutoxy]propionyloxy}phenyl 4-(4-*n*-alkoxyphenyl) benzoate (series B), and 4-{2(*S*)-[2(*S*)-methylbutoxy]propionyloxy}-4′-biphenyl 4-*n*-alkoxybenzoate (series C). Only one member of series A, 4-{2(*S*)-[2(*S*)-methylbutoxy]propionyloxy}phenyl 4-*n*-octyloxybenzoate (**5c**), exhibits a monotropic S_A phase. The *n*-alkoxy chain length at the biphenyl ring of series B has a remarkable efect on the S_C^* phase formation. An enantiotropic S_C^* phase can only be observed when the *n*-alkoxy chain is longer than the *n*-octyloxy group. The *n*-heptyloxy and *n*-octyloxy homologues exhibit a monotropic S_C^* phase. However, all members of series C possess an enantiotropic S_C^* phase. The occurrence of the phase sequence C–S_C^*–S_A–I or C–S_C^*–N*–I depends on the position of the biphenyl ring. The S_C^* phase temperature range in series B and C is up to 70°C.

1. Introduction

Ferroelectric liquid crystals (FLCs) have attracted considerable attention since their discovery in 1975 by Meyer *et al.* [1]. These materials are so influenced as solid-state ferroelectrics in an electric field that the dipole moments of the molecules align along the same direction macroscopically. The invention of the SSFLC (surface-stabilized FLC) light valve in 1980 by Clark and Lagerwall [2] opened the practical use of FLCs. Since then the optimization of the FLCs properties to improve the performance of SSFLC light valves has become a strong impulse for FLC materials research. In comparison with research on nematic liquid crystals research on FLC materials is still far from mature.

Natural products offer a lot of optically active compounds for preparing FLCs. Because the chemical procedures to manipulate hydroxy and carboxy groups are well-known in chemistry (*S*)-lactic acid is often used as a starting material of FLCs. Different derivatives of lactic acid are therefore designed and synthesized [3–7]. Meanwhile FLCs having the structure skeleton of lactic acid can also possess novel properties, i.e. S_C^* phase at room temperature [5,6] or high P_s value [3,4]. During the course of research on FLCs we were interested in chiral propionic acids which can be

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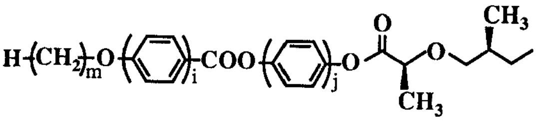
prepared by the etherification of the hydroxy group of (*S*)-lactic acid and chiral compounds. These chiral organic acids contain two centres of chirality. In addition to the absolute configuration of (*S*)-lactic acid the second chirality of these organic acids is transferred from the chirality of those added chiral compounds. Such chiral organic acids are still unknown in chemistry to the best of our knowledge. It is helpful for FLC materials research to know the effect of the second chirality on the formation of liquid crystal phases. To study the effect a new chiral propionic acid **2** was prepared. It was used as a chiral building block for synthesizing FLCs. Three series of chiral compounds containing **2**, A, B, and C, were prepared and their liquid crystal phase behaviour investigated. The results are reported in this paper.



Series A i = j = 1
Series B i = 2, j = 1
Series C i = 1, j = 2

2. Synthesis

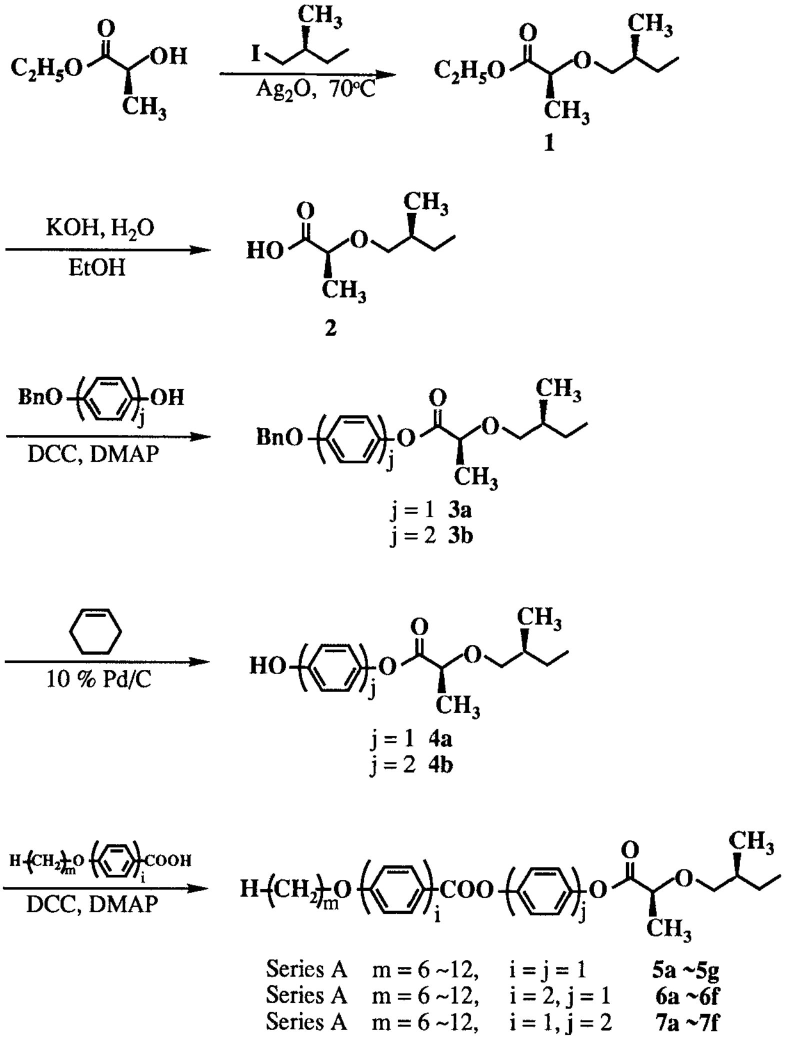
The synthesis of new FLCs was realized by the combination of aromatic carboxylic acids and new chiral compounds **4a** or **4b**. The synthetic sequence is shown in the scheme. The new chiral propionic acid ester **1** was prepared by the etherification of natural ethyl lactate with (*S*)-1-iodo-2-methylbutane in the presence of Ag_2O. Instead of stirring an ultrasonic condition was used here. After saponification of **1** the new chiral propionic acid **2** was formed easily.

The esterification of **2** with hydroquinone monobenzyl ether or 4,4′-biphenol monobenzyl ether and the cleavage of the benzyl group by hydrogenation gave the chiral compounds **4a** and **4b** in good yield. A catalytic transfer hydrogenation [8] was used here to cleave the benzyl ethers. Three series of chiral compounds, A, B, and C, were synthesized from **4a** or **4b** and the corresponding aromatic carboxylic acids under a standard reaction condition [9].

3. Results and discussion

An H-shift product was isolated during the etherification of ethyl lactate with (*S*)-1-iodo-2-methylbutane in the presence of Ag_2O. The side product formed in *c*. 10 per cent yeild could be removed by flash chromatography. The separation of the H-shift product became easier after the saponification reaction. No epimerization of new chiral compounds synthesized occurred during the whole synthetic route. All new compounds were characterized by IR, ^1H NMR, ^{13}C NMR, and MS. They also gave satisfactory elemental analyses.

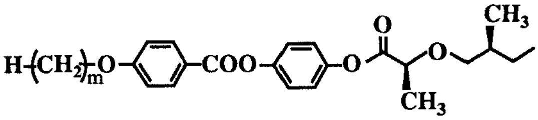
The number and position of the phenyl or biphenyl ring at the core part of the liquid crystals was modified in order to study the influence of the second chirality on the formation of the liquid crystal phases. Three series of chiral compounds, A, B, and C, were synthesized and investigated. Their liquid crystal phases and phase transition temperatures were identified by differential scanning calorimetry and



polarizing microscopy. The results of series A, B, and C are summarized in tables 1, 2, and 3, respectively. The specific rotation for each compound is also included in the corresponding table. Only one member of series A, **5c**, exhibits a liquid crystal phase, a monotropic S_A phase, it also has the lowest melting point among the whole series.

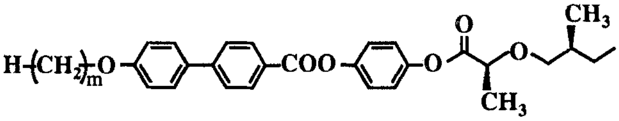
The results of **5c** points positively that the liquid crystal formation for a molecule containing the structure of **2** is possible. Therefore one of two phenyl rings in series A was replaced by a biphenyl ring. Following the similar chemical procedures as in series A, series B and C were prepared without any problem. The results are encouraging. In addition to other liquid crystal phases, S_C^* phases were observed in both series. The position of the biphenyl ring has a profound effect on the occurrence of liquid crystal phases. While series B gave a S_A phase on heating the S_C^* phase to the isotropic phase, series C gave a N* phase. The texture identification of the N* phases of **7a**, **7b**, and **7c** implies that these three compounds may have blue phases (BP). The alkoxy chain length has a remarkable influence on the liquid

Table 1. Phase transition temperatures and specific rotations of compounds **5a**–**5g**.



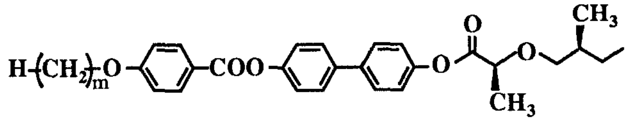
Compound	*m*	Phase transition temperature/°C	$[\alpha]^{28}_{D}$(CHCl$_3$)
5a	6	$C \xrightleftharpoons{66{\cdot}7} I$	−34°
5b	7	$C \xrightleftharpoons{51{\cdot}6} I$	−35°
5c	8	$C \xrightarrow{36{\cdot}6} I$, $I \xrightarrow{29{\cdot}4} S_A$, $S_A \xrightarrow{16{\cdot}9} C$	−33°
5d	9	$C \xrightleftharpoons{42{\cdot}0} I$	−36°
5e	10	$C \xrightleftharpoons{47{\cdot}4} I$	−33°
5f	11	$C \xrightleftharpoons{50{\cdot}8} I$	−36°
5g	12	$C \xrightleftharpoons{55{\cdot}6} I$	−31°

Table 2. Phase transition temperatures and specific rotations of compounds **6a**–**6f**.



Compound	*m*	Phase transition temperature/°C	$[\alpha]^{28}_{D}$ (CHCl$_3$)
6a	6	$C \xrightarrow{111{\cdot}7} S_B \xrightleftharpoons[106{\cdot}3]{160{\cdot}0} S_A \xrightleftharpoons[168{\cdot}5]{170{\cdot}0} I$, $S_B \xrightarrow{94{\cdot}0} S_?$, $S_? \xrightarrow{75{\cdot}0} C$	−33°
6b	7	$C \xrightleftharpoons[84.0]{102{\cdot}4} S_B \xrightarrow{120{\cdot}0} S_A \xrightleftharpoons[163{\cdot}0]{168{\cdot}5} I$, $S_A \xrightarrow{115{\cdot}0} S_C^*$, $S_C^* \xrightarrow{90{\cdot}0} S_B$	−32°
6c	8	$C \xrightleftharpoons[78{\cdot}1]{79{\cdot}8} S_B \xrightarrow{85{\cdot}1} S_A \xrightleftharpoons[158{\cdot}0]{160{\cdot}0} I$, $S_A \xrightarrow{129{\cdot}2} S_C^*$, $S_C^* \xrightarrow{117{\cdot}0} S_B$	−32°
6d	9	$C \xrightleftharpoons[69{\cdot}0]{75{\cdot}2} S_C^* \xrightleftharpoons[137{\cdot}5]{139{\cdot}6} S_A \xrightleftharpoons[157{\cdot}1]{158{\cdot}1} I$	−30°
6e	10	$C \xrightleftharpoons[70{\cdot}5]{76{\cdot}0} S_C^* \xrightleftharpoons[137{\cdot}0]{139{\cdot}0} S_A \xrightleftharpoons[153{\cdot}9]{154{\cdot}9} I$	−30°
6f	12	$C \xrightleftharpoons[75{\cdot}0]{81{\cdot}8} S_C^* \xrightleftharpoons[136{\cdot}0]{137{\cdot}1} S_A \xrightleftharpoons[148{\cdot}0]{149{\cdot}0} I$	−30°

Table 3. Phase transition temperatures and specific rotations of compounds **7a**–**7f**.



Compound	*m*	Phase transition temperature/°C	$[\alpha]_D^{28}$ (CHCl$_3$)
7a	6	$\mathrm{C} \xrightarrow{51\cdot5} \mathrm{S_C^*} \underset{117\cdot9}{\overset{121\cdot2}{\rightleftharpoons}} \mathrm{N^*} \xrightarrow{142\cdot0} \mathrm{I}$ $\mathrm{S_C^*} \xrightarrow{46\cdot7} \mathrm{S_?} \xrightarrow{36\cdot0} \mathrm{C}$; $\mathrm{I} \xrightarrow{138\cdot9} \mathrm{BP} \xrightarrow{127\cdot0} \mathrm{N^*}$	−33°
7b	7	$\mathrm{C} \xrightarrow{64\cdot1} \mathrm{S_C^*} \underset{121\cdot2}{\overset{124\cdot2}{\rightleftharpoons}} \mathrm{N^*} \xrightarrow{137\cdot5} \mathrm{I}$ $\mathrm{S_C^*} \xrightarrow{45\cdot6} \mathrm{S_?} \xrightarrow{35\cdot9} \mathrm{C}$; $\mathrm{I} \xrightarrow{134\cdot5} \mathrm{BP} \xrightarrow{127\cdot3} \mathrm{N^*}$	−37°
7c	8	$\mathrm{C} \underset{72.2}{\overset{84\cdot8}{\rightleftharpoons}} \mathrm{S_C^*} \underset{124\cdot9}{\overset{127\cdot2}{\rightleftharpoons}} \mathrm{N^*} \xrightarrow{137\cdot6} \mathrm{I}$ $\mathrm{I} \xrightarrow{135\cdot3} \mathrm{BP} \xrightarrow{128\cdot3} \mathrm{N^*}$	−34°
7d	9	$\mathrm{C} \underset{70\cdot6}{\overset{81\cdot9}{\rightleftharpoons}} \mathrm{S_C^*} \underset{124\cdot9}{\overset{127\cdot6}{\rightleftharpoons}} \mathrm{N^*} \underset{131\cdot2}{\overset{133\cdot8}{\rightleftharpoons}} \mathrm{I}$	−32°
7e	10	$\mathrm{C} \underset{72\cdot5}{\overset{82\cdot5}{\rightleftharpoons}} \mathrm{S_C^*} \underset{126\cdot7}{\overset{129\cdot8}{\rightleftharpoons}} \mathrm{N^*} \underset{130\cdot8}{\overset{134\cdot0}{\rightleftharpoons}} \mathrm{I}$	−31°
7f	12	$\mathrm{C} \underset{65\cdot5}{\overset{76\cdot0}{\rightleftharpoons}} \mathrm{S_C^*} \underset{123\cdot3}{\overset{127\cdot0}{\rightleftharpoons}} \mathrm{N^*} \underset{125\cdot2}{\overset{129\cdot0}{\rightleftharpoons}} \mathrm{I}$	−33°

crystal phase formation for series B, but not for series C. The compounds **6a**, **6b**, and **6c** exhibit enantiotropic S_B and S_A phases. Although a S_C^* phase can be observed for **6b** and **6c**, it is monotropic. An enantiotropic S_C^* phase was formed only when the alkoxy chain length was increased to a *n*-nonyloxy group or longer. The thermal stability of the S_C^* phases observed is high. It ranges between 55°C and 65°C. However, almost no change of the liquid crystal phases within series C was observed when the alkoxy chain length was varied. The thermal stability of the S_C^* phase in this series is also good. Among them the compound **7a** possesses the best thermal stability of the S_C^* phase, with a range of 70°C.

The chiral propionic acid **2** containing two centres of chirality has been successfully used as a chiral building block for synthesizing liquid crystals, especially FLCs. The results indicate the new chiral acid **2** seems useful for the formation of S_C^* materials, and could be very helpful for preparing new ferroelectric liquid crystal materials and possibly also ferroelectric liquid crystal side chain polymers. The results also suggest that other similar chiral organic acids derived from natural lactic acid could be as promising as **2** for the preparation of new ferroelectric liquid crystal materials.

4. Experimental

(*S*)-1-Iodo-2-methylbutane was purchased from Aldrich. Commericially available chemical reagents and solvents were used directly without further purification. Lobar column (Lichroprep Si 60) from Merck was used for middle pressure liquid chromatography (MPLC). Infrared and NMR spectra were recorded on a Nicolet FTIR and a Varian Gemini 200 spectrometer, respectively. NMR chemical shifts are given in parts per million relative to tetramethylsilane (TMS). Mass spectra were recorded on a VG 70-250S instrument. Elemental analyses were made by a Heraeus combustion apparatus. Values of specific rotation were measured by a Jasco DIP 370 polarimeter. Phase transition temperatures and textures of liquid crystal phases were determined by differential scanning calorimetry using a Seiko SSC 5000 DSC system and a Nikon Microphot-FXA polarizing microscope in conjunction with a Mettler FP 52 hot stage, respectively.

4.1. *Ethyl 2(S)-[2(S)-methylbutoxy]propionate* (**1**)

To a mixture of 5·9 g (50 mmol) of (*S*)-ethyl lactate and 13·9 g (60 mmol) of (*S*)-1-iodo-2-methylbutane, 13·9 g (60 mmol) of silver oxide was added and reacted at 70°C in an ultrasonic bath for 14 h. The product was extracted with diethyl ether (5 × 80 ml), and the ether phase was washed by 5 per cent KOH (2 × 100 ml) and then by water (2 × 100 ml). The organic phase was collected and dried over $MgSO_4$. Filtration and removal of solvent by a rotatory evaporator gave 5·8 g of crude product which was purified by MPLC (hexane/ethyl acetate, 15/1), affording 3·5 g (39 per cent) of ester **1** as a colourless liquid. IR (neat) 2962, 1752, 1462, 1373, 1269, 1133, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) 4·15 (q, 2 H, $J = 7{\cdot}0$ Hz), 3·85 (q, 1 H, $J = 6{\cdot}8$ Hz), 3·39 (AB d, 1 H, $J = 8{\cdot}8$, 6·1 Hz), 3·06 (AB d, 1 H, $J = 8{\cdot}8$, 6·8 Hz), 1·65 (m, 1 H), 1·45 (m, 1 H), 1·34 (d, 3 H, *J*-6·8 Hz), 1·23 (t, 3 H, J = 7·1 Hz), 1·11 (m, 1 H), 0·84 (peaks overlapped, 6 H); ^{13}C NMR ($CDCl_3$) 173·5, 75·5, 75·1, 60·6, 35·0, 26·0, 18·6, 16·4, 14·1, 11·1; MS (*m/z* (relative intensity): 187 ($M^+ - 1$, 3·0); $[\alpha]_D^{28} = -54°$ ($CHCl_3$, $c = 1{\cdot}02$). Elemental analysis for $C_{10}H_{20}O_3$: calculated C: 63·79 per cent, H: 10·71 per cent; found C: 63·64 per cent, H: 10·62 per cent.

4.2. *2(S)-[2(S)-methylbutoxy]propionic acid* (**2**)

To a solution of 3·3 g (18 mmol) of **1** in 20 ml of ethyl alcohol was added a solution of 2·2 g (40 mmol) of KOH in 80 per cent ethyl alcohol. After refluxing for 1·5 h the ethyl alcohol was removed. The residue was acidified by conc. HCl at 0°C. After extraction with CH_2Cl_2 (4 × 100 ml) the organic layer was dried over $MgSO_4$. Filtration and removal of solvent gave 2·7 g (93 per cent) of acid **2** as a colourless viscous oil. IR (neat) 3162 (broad), 2880, 1727, 1459, 1376, 1240, 1132, 1068 cm^{-1}; ^1H NMR ($CDCl_3$) 3·95 (q, 1 H, $J = 6{\cdot}9$ Hz), 3·46 (AB d, 1 H, $J = 8{\cdot}8$, 6·1 Hz), 3·18 (AB d, 1 H, $J = 8{\cdot}8$, 6·8 Hz), 1·65 (m, 1 H), 1·48 (m, 1 H), 1·44 (d, 3 H, $J = 6{\cdot}9$ Hz), 1·16 (m, 1 H), 0·88 (peaks overlapped, 6 H); ^{13}C NMR ($CDCl_3$) 178·7, 75·7, 74·7, 34·9, 26·0, 18·2, 16·4, 11·2; MS *m/z* (relative intensity): 161 ($M^+ + 1$, 11·5); $[\alpha]_D^{28} = -22°$ ($CHCl_3$, $c = 1{\cdot}03$). Elemental analysis for $C_8H_{16}O_3$: calculated C: 59·97 per cent, H: 10·07 per cent; found C: 59·52 per cent, H: 10·04 per cent.

4.3. *4-Benzoxyphenyl and 4,4′-benzoxybiphenyl 2(S)-[2(S)-methylbutoxy]propionate* (**3a**), (**3b**)

A solution of 1·6 g (10 mmol) of **2**, 11 mmol of hydroquinone monobenzyl ether or 4,4′-biphenol monobenzyl ether, 0·12 g (1 mmol) of 4-(*N*, *N*-dimethylamino)-pyridine (DMAP), and 2·3 g (11 mmol) of dicyclohexylcarbodiimide (DCC) in 25 ml of $CHzCl_2$ were stirred under N_2 at room temperature for 10–14 h. The precipitate was filtered off. The filtrate was concentrated and purified by MPLC (hexane/ethyl acetate, 4/1). The pure product **3a** or **3b** was obtained in 75–80 per cent yield.

(**3a**: IR (KBr) 2936, 1763, 1505, 1244, 1189, 1012, 879, 744 cm^{-1}; ^{1}H NMR ($CDCL_3$) 7·38 (m, 5 H), 7·0 (dd, 4 H, J=6·7 Hz), 5·04 (s, 2 H), 4·14 (q, 1 H, J=6·8 Hz), 3·53 (AB d, 1 H, J=8·7, 6·1 Hz), 3·25 (AB d, 1 H, J=8·7, 6·7 Hz), 1·71 (m, 1 H), 1·55 (d, 3 H, J=6·8 Hz), 1·50 (m, 1 H), 1·20 (m, 1 H) 0·92 (peaks overlapped, 6 H); ^{13}C NMR ($CDCl_3$) 172·4, 156·5, 144·1, 136·7, 128·6 (2 C), 128·0, 127·4 (2 C), 122·1 (2 C), 115·4 (2 C), 75·9, 75·2, 70·1, 35·1, 26·1, 18·6, 16·5, 11·2; MS m/z (relative intensity): 342 (M^+, 2·8); $[\alpha]_D^{28} = -51°$ ($CHCl_3$, c=1·0); mp 52·5°C. Elemental analysis for $C_{21}H_{26}O_4$: calculated C: 73·66 per cent, H: 7·65 per cent, found C: 73·67 per cent, H: 7·62 per cent.

(**3b**):IR (KBr) 2974, 2882, 1765, 1495, 1450, 1376, 1132, 808, 729 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7·48 (m,9 H), 7·14 (d, 2 H, J=6·7 Hz), 7·03 (d, 2 H, J=6·7 Hz), 5·10 (s, 2 H), 4·18 (q, 1 H, J=6·8 Hz), 3·58 (AB d, 1 H, J=8·7, 6·1 Hz), 3·26 (AB d, 1 H, J=8·7, 6·7 Hz), 1·75 (m, 1 H), 1·60 (d, 3 H, J=6·8 Hz), 1·55 (m, 1 H), 1·20 (m, 1 H), 0·93 (peaks overlapped, 6 H); ^{13}C NMR ($CDCl_3$) 172·2, 158·4, 149·4, 138·7, 136·9, 133·1, 128·6 (2 C), 128·2 (2 C), 128·0, 127·7 (2 C), 127·5 (2 C), 121·5 (2 C), 115·2 (2 C), 75·8, 75·2, 70·1, 35·1, 26·1, 18·7, 16·5, 11·3; MS m/z (relative intensity): 418 (M^+, 7·0); $[\alpha]_D^{28} = -48°$ ($CHCl_3$, c=1·0); mp 120·3°C. Elemental analysis for $C_{27}H_{30}O_4$: calculated C: 77·48 per cent, H: 7·22 per cent; found C: 77·52 per cent, H: 7·22 per cent.

4.4. *Hydroxyphenyl and 4,4′-hydroxybiphenyl 2(S)-[2(S)-methylbutoxy]propionate* (**4a**), (**4b**)

The known procedure for the cleavage of the benzyl group was used [8]. A mixture of 10 mmol of **3a** or **3b**, 80 ml of ethyl alcohol, 40 ml of cyclohexene, and 0·8 g of Pd/C were heated under reflux for 1–2 h (monitored by TLC). Filtration and removal of solvent gave crude product in 95 per cent yield. The product is usually pure enough for the next reaction. It could be further purified by MPLC (hexane/ethyl acetate, 4/1).

(**4a**): Viscous oil. IR (neat) 3440, 2877, 1753, 1602, 1507, 1190, 825, 769 cm^{-1}; ^{1}H NMR ($CDCl_3$) 6·90 (d, 2 H, J=8·8 Hz), 6·75 (d, 2 H, J=8·8 Hz), 4·15 (q, 1 H, J=6·9 Hz), 3·56 (AB d, 1 H, J=8·8, 6·1 Hz), 3·24 (AB d, 1 H, J=8·8, 6·7 Hz), 1·75 (m, 1 H), 1·54 (d, 3 H, J=6·9 Hz), 1·55 (m, 1 H), 1·15 (m, 1 H) 0·90 (peaks overlapped, 6 H); ^{13}C NMR ($CDCl_3$) 173·1, 153·8, 143·4, 122·0 (2 C), 116·1 (2 C), 75·9, 75·2, 35·0, 26·0, 18·6, 16·4, 11·2; MS m/z (relative intensity): 252 (M^+, 2·0); $[\alpha]_D^{28} = -54°$ ($CHCl_3$, c=2·1). Elemental analysis for $C_{14}H_{20}O_4$: calculated C: 66·65 per cent, H: 7·99 per cent; found C: 66·28 per cent, H: 8·02 per cent.

(**4b**): IR (KBr) 3494, 2878, 1735, 1609, 1168, 1068, 834, 809 cm^{-1}; ^{1}H NMR ($CDCl_3$) 7·50 (d, 2 H, J=8·7 Hz), 7·35 (d, 2 H, J=8·7 Hz), 7·12 (d, 2 H, J=6·6 Hz), 6·84 (d, 2 H, J=6·6 Hz), 4·19 (q, 1 H, J=6·9 Hz), 3·59 (AB d, 1 H, J=8·8, 6·1 Hz), 3·27 (AB d, 1 H, J=8·8, 6·7 Hz), 1·75 (m, 1 H), 1·59 (d, 3 H, J=6·9 Hz), 1·51 (m, 1 H), 1·20 (m, 1 H), 0·94 (peaks overlapped, 6 H); ^{13}C NMR ($CDCl_3$) 172·5, 155·3, 149·3, 138·8, 132·8, 128·3 (2 C), 127·7 (2 C), 121·5 (2 C), 115·7 (2 C), 75·9, 75·3, 35·1, 26·1, 18·7, 16·6, 11·3; MS m/z (relative intensity): 328 (M^+, 3·2); $[\alpha]_D^{28} = -53°$ ($CHCl_3$, c=1·0); mp 142·1°C. Elemental analysis for $C_{20}H_{24}O_4$: calculated C: 73·15 per cent, H: 7·37 per cent; found C: 73·71 per cent, H: 7·26 per cent.

4.5. *4-{2(S)-[2(S)-methylbutoxy]propionyloxy}phenyl 4-n-octanoxybenzoate* (**5c**)

A solution of 10 mmol of the *n*-octanyloxybenzoic acid, 11 mmol of DCC, 11 mmol of the phenol **4a**, and 1 mmol of DMAP in 25 ml of CH_2Cl_2 was stirred at room temperature for 14 h. The precipitate was removed by filtration. Removal of solvent, purified by MPLC (hexane/ethyl acetate, 4/1), and recrystallization from hexane gave the product as a white solid in 70 per cent yield. IR (KBr) 2960, 1768, 1732, 1611, 1505, 1186, 1071, 890, 845, 763 cm^{-1}; ^{1}H NMR ($CDCl_3$) 8·11 (d, 2 H, J = 8·8 Hz), 7·18 (m, 4 H), 6·96 (d, 2 H, J = 8·8 Hz), 4·16 (q, 1 H, J = 6·9 Hz), 4·03 (t, 2 H, J = 6·4 Hz), 3·56 (AB d, 1 H, J = 8·8, 6·1 Hz), 3·24 (AB d, 1 H, J = 8·8, 6·6 Hz), 1·8–1·1 (peaks overlapped, 18 H), 0·88 (peaks overlapped, 9 H); ^{13}C NMR ($CDCl_3$) 171·9, 164·7, 163·6, 148·5, 147·8, 132·3 (2 C), 122·7 (2 C), 122·2 (2 C), 121·2, 114·3 (2 C), 75·8, 75·2, 68·3, 35·1, 31·8, 29·3, 29·2, 29·1, 26·1, 25·9, 22·6, 18·6, 16·5, 14·1, 11·2; MS m/z (relative intensity): 484 (M^+, 9·0); $[\alpha]_D^{28} = -33°$($CHCl_3$, $c = 1·02$). Elemental analysis for $C_{29}H_{40}0_6$: calculated C: 71·87 per cent, H: 8·32 per cent; found C: 71·69 per cent, H: 8·34 per cent.

4.6. *4-{2(S)-[2(S)-methylbutoxy]propionyloxy}phenyl 4-(4-n-alkoxyphenylbenzoate* (6a)-(6f)

The esterification procedure used was similar to that in section 4.5. The mobile phase for MPLC was hexane/ethyl acetate/chloroform (6/1/2). Recrystallization from hexane gave a white solid in 60–70 per cent yield.

(**6f**): IR (KBr) 2919, 1763, 1732, 1603, 1503, 1293, 832, 764 cm^{-1}; ^{1}H NMR ($CDCl_3$) 8·23 (d, 2 H, J = 8·4 Hz), 7·65 (d, 4 H, J = 8·5 Hz), 7·25 (m, 4 H), 7·02 (d, 2 H, J = 8·8 Hz), 4·18 (q, 1 H, J = 6·8 Hz), 4·02 (t, 2 H, J = 6·5 Hz), 3·57 (AB d, 1 H, J = 8·8, 6·1 Hz), 3·26 (AB d, 1 H, J = 8·8, 6·6 Hz), 1·9–1·1 (peaks overlapped, 26 H), 0·92 (peaks overlapped, 9 H); ^{13}C NMR ($CDCl_3$) 172·0, 165·0, 159·6, 148·5, 147·9, 146·1, 131·9, 130·8 (2 C), 128·4 (2 C), 127·2, 126·6 (2 C), 122·7 (2 C), 122·3 (2 C), 115·0 (2 C), 75·9, 75·2, 68·2, 35·1, 31·9, 29·7 (2 C), 29·6 (2 C), 29·4 (2 C), 29·3, 26·2, 26·0, 22·7, 18·7, 16·5, 14·2, 11·3; MS m/z (relative intensity): 617 ($M^+ + 1$, 1·8); $[\alpha]_D^{28} = -30°$ ($CHCl_3$, $c = 1·01$). Elemental analysis for $C_{39}H_{52}0_6$: calculated C: 75·94 per cent, H: 8·50 per cent; found C: 76·11 per cent, H: 8·47 per cent.

4.7. *4-{2(S)-[2(S)-methylbutoxy]propionyloxy}-4′-biphenyl-4-n-alkoxybenzoate* (7a)-(7f)

The preparation procedure and the mobile phase for MPLC were identical to that is sections 4.5 and 4.6 respectively. Recrystallization from hexane gave white solid in 60–70 per cent yield.

(**7f**): IR (KBr) 2850, 1770, 1729, 1610, 1494, 1168, 845, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$) 8·15 (d, 2 H, J = 6·8 Hz), 7·59 (d, 4 H, J = 7·6 Hz), 7·23 (d, 4 H, J = 7·6 Hz), 6·98 (d, 2 H, J = 6·8 Hz), 4·19 (q, 1 H, J = 6·8 Hz), 4·04 (t, 2 H, J = 6·4 Hz), 3·59 (AB d, 1 H, J = 8·8, 6·1 Hz), 3·25 (AB d, 1 H, J = 8·8, 6·6 Hz), 1·93–1·1 (peaks overlapped, 26 H), 0·93 (peaks overlapped, 9 H); ^{13}C NMR ($CDCl_3$) 172·1, 164·9, 163·5, 150·6, 149·9, 138·3, 137·8, 132·3 (2 C), 128·1 (4 C), 122·1 (2 C), 121·6 (2 C), 121·4, 114·3 (2 C), 75·9, 75·2, 68·3, 35·1, 31·9, 29·6 (2 C), 29·5 (2 C), 29·3 (2 C), 29·1, 26·1, 25·9, 22·6, 18·6, 16·5, 14·1, 11·3; MS m/z (relative intensity): 616 (M^+, 2·7); $[\alpha]_D^{28} = -33°$ ($CHCl_3$, $c = 0·95$). Elemental analysis for $C_{39}H_{52}0_6$: calculated C: 75·94 per cent, H: 8·50 per cent; found C: 76·02 per cent, H: 8·37 per cent.

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References

[1] Meyer, R. B., Liebert, L., Strzelecki, L., and Keller, P., 1975, *J. Phys. Lett., Paris*, **36,** 69.

[2] Clark, N. A., and Lagerwall, S. T., 1980, *Appl. Phys. Lett.*, **36,** 899.

[3] Taniguchi, H., Ozaki, M., Yoshino, K., Yamasaki, N., and Satoh, K., 1987, *Jap. J. appl. Phys.*, **26,** L1558.

[4] Bone, M. F., Constant, M. J., Gemmell, P. A., Gray, G. W., Lancey, D., and Toyne, K. J., 1988, *Molec. Crystals liq. Crystals,* **164,** 117.

[5] Walba, D. M., Slater, S. C., Thurmes, W. N., Clark, N. A., Handschy, M. A., and Supon, F., 1986, *J. Am. chem. Soc.*, **108,** 5210.

[6] Otterholm, B., Alstermark, C., Flatischler, K., Dahlgren, A., Lagerwall, S. T., and Skarp, K., 1987, *Molec. Crystals liq. Crystals,* **146,** 189.

[7] Liang, J. C., and Kumar, S., 1988, *Molec. Crystals liq. Crystals*, **159,** 115.

[8] Hanessian, S., Liak, T. J., and Vanasse, B., 1981, *Synthesis,* 396.

[9] Hassner, A., and Alexanian, V., 1978, *Tetrahedron Lett.*, **46,** 4475.