Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Ferroelectric liquid crystal materials synthesized from 2(*S*)-[2(*S*)-methylbutyloxy]propanol

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To cite this Article Tsai, W. L. and Yang, S. H.(1993) 'Ferroelectric liquid crystal materials synthesized from 2(*S*)-[2(*S*)-methylbutyloxy]propanol', Liquid Crystals, 14: 3, 661 — 666
To link to this Article: DOI: 10.1080/02678299308027745
URL: http://dx.doi.org/10.1080/02678299308027745

LIQUID CRYSTALS, 1993, VOL. 14, NO. 3, 661–666

Ferroelectric liquid crystal materials synthesized from 2(*S*)-[2(*S*)-methylbutyloxy]propanol

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A new chiral alcohol, 2(*S*)-[2(*S*)-methylbutyloxy]propanol (**3**), containing two chiral centres has been synthesized from ethyl lactate and (*S*)-1-iodo-2-methylbutane. It was used as a chiral building block for the preparation of ferroelectric liquid crystal materials. Several of the new materials exhibit an enantiotropic S_C^* phase with a wide temperature range. The results indicate that the molecular structure of **3** is useful for synthesizing ferroelectric liquid crystal materials.

1. Introduction

Since the discovery of ferroelectric liquid crystals by Meyer *et al.* [1] and the invention of the surface-stabilized ferroelectric liquid crystal light valve by Clark and Lagerwall [2], the preparation and optimization of ferroelectric liquid crystal materials to improve the performance of the surface stabilized ferroelectric liquid crystal light valve has become an important research field in both pure and applied science. The unique advantages of ferroelectric liquid crystals in switching performance and memorising capability have made such liquid crystals very important in display and switching devices.

Optically active natural products are often used as starting materials for synthesizing novel compounds particularly chiral liquid crystals. Because it contains two easily convertible functional groups, natural lactic acid is one of the most used natural products for synthesizing ferroelectric liquid crystals [3, 4]. Therefore, chiral alcohols derived from lactic acid have been designed and synthesized [5–7] to optimize ferroelectric liquid crystal properties. They all contain only one chiral centre. But chiral alcohols in which a second chiral centre is formed by the etherification of α-hydroxy group of lactic acid with a chiral compound are still unknown in the fields of both chemistry and liquid crystals. It would be helpful for the design of new ferroelectric liquid crystals if the influence of the second chiral centre on the formation of liquid crystal phases were known. In order to study such an effect, this paper examines the synthesis of a new chiral alcohol, 2(*S*)-[2(*S*)-methylbutyloxy]propanol **3** and its applications for the preparation of ferroelectric liquid crystals.

2. Synthesis

The chiral liquid crystal materials designed for this study were formed by the combination of a substituted chiral phenol moiety and an aromatic carboxylic acid. The synthesis of new chiral derivatives and ferroelectric liquid crystals is shown in the scheme. New chiral compound (**2**) was synthesized from ethyl lactate (**1**) and (*S*)-1-iodo-2-methylbutane in the presence of Ag_2O. New chiral alcohol (**3**) was formed by the

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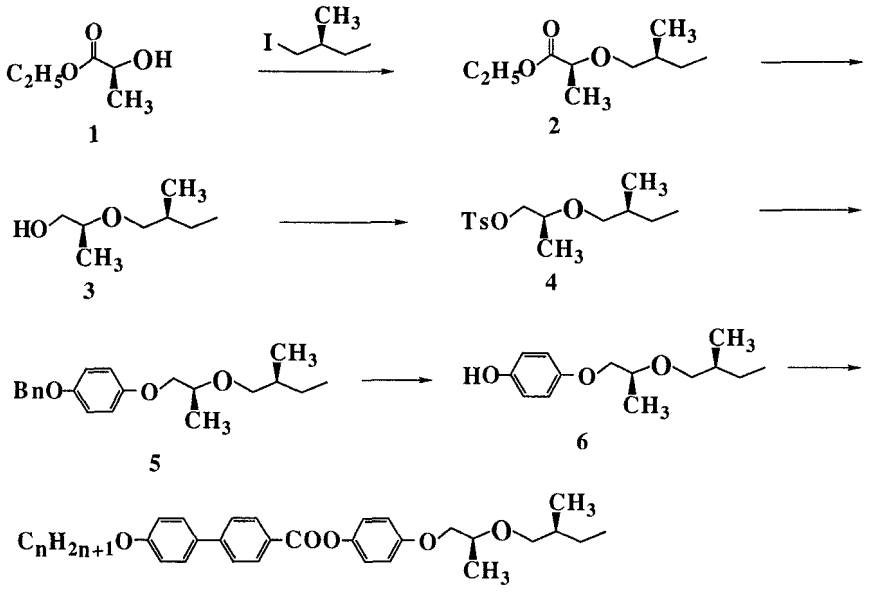

7 – 14 (n = 4 – 12)

reduction of (**2**) in high yield. The tosylation of (**3**) gave the toluenesulphonate (**4**) quantitatively. Compound (**5**) was prepared by the etherification of (**4**) with hydroquinone monobenzyl ether. Deprotection of the benzyl group by hydrogenation gave chiral compound (**6**) in good yield. Details of the synthetic procedures will be published separately [8].

Liquid crystal materials (**7–14**) were synthesized from (**6**) and the corresponding 4-(4-*n*-alkoxyphenyl) benzoic acid, following a standard reaction procedure [9].

3. Results and discussion

No epimerization of the new chiral compounds was observed during the whole synthetic sequence. All new compounds were characterized by IR, ^{1}H-NMR, ^{13}C-NMR, and MS; they also gave satisfactory elemental analyses.

The liquid crystal phases and phase transition temperatures of the compounds (**7–14**) are summarized in the table. Only compound (**7**) of the series possessed a monotropic S_E phase. No S_C^* phase was found in the liquid crystal materials (**7–10**). They exhibited only enantiotropic S_B and S_A phases. The phase transition temperatures decreased gradually as the length of the alkoxy chain at biphenyl ring increased. A S_C^* phase was first observed for compound (**11**), when the alkoxy chain at the biphenyl ring was *n*-octyloxy. Both S_B and S_A phases were also formed. The S_B phase was eliminated in ferroelectric liquid crystal materials (**12–14**) which exhibited wide temperature range S_C^* phases, as well as S_A phases. Both liquid crystal phases are enantiotropic. For these three ferroelectric liquid crystal materials, the second chiral centre added in this way does not eliminate the S_C^*–S_A phase sequence which has normally been found for this core and *n*-alkoxy chain system. No higher ordered smectic phases were observed among these three ferroelectric liquid crystal materials (**12–14**). A similar ferroelectric liquid crystal material in the literature [7], but without the second centre of chirality as

in (**12**), exhibited a highly ordered smectic phase in addition to the S_C^* and S_A phases. Therefore, the second chiral centre formed in this way could broaden the usage of lactic acid in liquid crystal materials research.

The results indicate the new chiral alcohol (**3**) 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 molecules derived from natural lactic acid, which are now under intensive study, could be as promising as (**3**) for the preparation of new ferroelectric liquid crystal materials.

4. Experimental

N,*N*-Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), and packing material for flash chromatography were purchased from Merck. All solvents (HPLC grade) obtained from Fisher were used without further purification. Infrared and NMR spectra were recorded using a Nicolet FTIR and a Varian Gemini 200 spectrometer respectively. Elemental analyses were obtained using a Heraeus CHN-O-RAPID combustion apparatus. Mass spectra were recorded on a JMS-D100 instrument. Specific rotations were measured with a Jasco DIP-710 polarimeter. Textures and transition temperatures of the liquid crystal phases were determined using a Nikon Microphot-FXA polarizing microscope, in conjunction with a Mettler FP82 heating stage, and a SEIKO DSC200 differential scanning calorimeter.

The following esterification procedure, adapted from the literature [9], was used to prepare compounds (**7–14**). A solution of 4-(4-*n*-alkoxyphenyl)benzoic acid (0·1 mmol), substituted chiral phenol (**6**) [8] (0·11 mmol), DCC (0·2 mmol), and DMAP (0·01 mmol) in 5 ml of CH_2Cl_2 was stirred at room temperature until the reaction was complete (monitored by TLC). Filtration and removal of the solvent from the filtrate gave the crude product which was then purified by flash column chromatography (SiO_2, CH_2Cl_2/hexane = 1 : 1). The pure products (**7–14**) were obtained in 70–80 per cent yields.

Liquid crystal phases and phase transition temperatures of chiral compounds **7–14**.

Compound	*n*	Phase transition temperatures/°C
7	4	$C \overset{109}{\rightarrow} S_B \underset{116}{\overset{118}{\rightleftharpoons}} S_A \underset{177}{\overset{182}{\rightleftharpoons}} I$; $C \overset{65}{\rightarrow} S_E \overset{107}{\rightarrow} S_B$
8	5	$C \underset{93}{\overset{96}{\rightleftharpoons}} S_B \underset{108}{\overset{111}{\rightleftharpoons}} S_A \underset{166}{\overset{171}{\rightleftharpoons}} I$
9	6	$C \underset{92}{\overset{95}{\rightleftharpoons}} S_B \underset{109}{\overset{111}{\rightleftharpoons}} S_A \underset{165}{\overset{168}{\rightleftharpoons}} I$
10	7	$C \underset{73}{\overset{77}{\rightleftharpoons}} S_B \underset{97}{\overset{99}{\rightleftharpoons}} S_A \underset{150}{\overset{157}{\rightleftharpoons}} I$
11	8	$C \underset{60}{\overset{64}{\rightleftharpoons}} S_B \underset{89}{\overset{92}{\rightleftharpoons}} S_C^* \underset{116}{\overset{121}{\rightleftharpoons}} S_A \underset{154}{\overset{158}{\rightleftharpoons}} I$
12	9	$C \underset{69}{\overset{74}{\rightleftharpoons}} S_C^* \underset{128}{\overset{130}{\rightleftharpoons}} S_A \underset{148}{\overset{151}{\rightleftharpoons}} I$
13	10	$C \underset{54}{\overset{62}{\rightleftharpoons}} S_C^* \underset{110}{\overset{120}{\rightleftharpoons}} S_A \underset{137}{\overset{140}{\rightleftharpoons}} I$
14	12	$C \underset{56}{\overset{71}{\rightleftharpoons}} S_C^* \underset{127}{\overset{130}{\rightleftharpoons}} S_A \underset{137}{\overset{141}{\rightleftharpoons}} I$

4.1. *2(S)-[2(S)-methylbutyloxy]propanol* (**3**)

To a solution of 4·78 g (32·7 mmol) of (**2**) [10] in EtOH was added 3·88 g (102 mmol) of $NaBH_4$ and the mixture heated under reflux for 4·5 h. The mixture was cooled to room temperature, shaken with CH_2Cl_2/H_2O (1:1, 3 × 100 ml), and the organic extracts dried over Na_2SO_4. Filtration and removal of solvent by rotary evaporation gave the crude product which was purified by flash column chromatography (SiO_2, CH_2Cl_2/hexane 2:1), affording 3·68 g (77 per cent) of alcohol (**3**) as a colourless liquid, $[\alpha]_D^{25} = 15{\cdot}0°$ ($C = 1{\cdot}00$, EtOH). FTIR (neat): 3421, 2964, 2930, 2876, 1461, 1376, 1144, 1089, 1047 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0·87 (6 H, m), 1·07 (3 H, d), 1·12 (1 H, m), 1·50 (2 H, m), 2·10 (1 H, br s), 3·27 (2 H, m), 3·50 (3 H, m). ^{13}C NMR ($CDCl_3$): δ 11·87 (1 C), 16·36 (1 C), 17·24 (1 C), 26·84 (1 C), 35·85 (1 C), 66·99 (1 C), 74·62 (1 C), 76·42 (1 C). MS: 115 (M-31), 71, 18. The high volatility of (**3**) made elementary analysis difficult.

4.2. *4-{2(S)-[2(S)-methylbutyloxy]propoxy}phenyl 4-(4-butyloxyphenyl)benzoate* (**7**)

$[\alpha]_D^{25} = -15{\cdot}7°$ (C = 1·02, $CHCl_3$). FTIR (KBr): 3058, 2930, 1726, 1603, 1279, 1073, 821, 762 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0·88 (6 H, m), 0·98 (3 H, t), 1·15 (3 H, m), 1·26 (3 H, d), 1·55 (2 H, m), 1·80 (2 H, m), 3·37 (2 H, m), 3·80 (2 H, m), 4·0 (3 H, m), 6·69 (4 H, m), 7·12 (2 H, d), 7·62 (4 H, dd), 8·21 (2 H, d). ^{13}C NMR ($CDCl_3$): δ 12·09, 14·64, 17·38, 18·11, 20·04, 27·00, 32·08, 36·03, 68·60, 72·88, 74·72, 75·66, 115·75 (2 C), 116·04 (2 C), 123·21 (2 C), 127·32 (2 C), 128·38, 129·14 (2 C), 131·44 (2 C), 132·77, 145·30, 146·63, 157·48, 160·35, 166·25. MS: 490 (M^+), 253, 197, 71. Elemental anal. for $C_{31}H_{38}O_5$: calcd C: 75·92, H: 7·76; found C: 75·76, H: 7·82.

4.3. *4-{2(S)-[2(S)-methylbutyloxy]propoxy}phenyl 4-(4-pentyloxyphenyl)benzoate* (**8**)

$[\alpha]_D^{25} = -12{\cdot}7°$ (C = 1·02, $CHCl_3$). FTIR (KBr): 3080, 1933, 1730, 1605, 1278, 1074, 823, 764 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0·92 (9 H, m), 1·20 (1 H, m), 1·27 (3 H, d), 1·47 (6 H, m), 1·82 (2 H, m), 3·38 (2 H, m), 3·80 (2 H, m), 4·01 (3 H, m), 6·97 (4 H, m), 7·12 (2 H, d), 7·63 (4 H, dd), 8·22 (2 H, d). ^{13}C NMR ($CDCl_3$): δ 11·94, 14·67, 17·22, 17·97, 23·10, 26·85, 28·83, 29·58, 35·88, 68·77, 72·72, 74·57, 75·52, 115·60 (2 C), 115·89 (2 C), 123·06 (2 C), 127·18 (2 C), 128·22, 128·99 (2 C), 131·29 (2 C), 132·63, 145·15, 146·49, 157·32, 160·19, 166·11. MS: 504 (M^+), 267, 197. Elemental anal. for $C_{32}H_{40}O_5$: calcd C: 76·19, H: 7·94; found C: 76·32, H: 8·06.

4.4. *4-{2(S)-[2-(S)-methylbutyloxy]propoxy}phenyl 4-(4-hexyloxyphenyl)benzoate* (**9**)

$[\alpha]_D^{25} = -10{\cdot}7°$ (C = 1·05, $CHCl_3$). FTIR (KBr): 2958, 2873, 1730, 1603, 1510, 1250, 1073 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0·86 (9 H, m), 1·15 (1 H, m), 1·25 (3 H, d), 1·50 (8 H, m), 1·79 (2 H, m), 3·36 (2 H, m), 3·8 (2 H, m), 4·0 (3 H, m), 6·95 (4 H, m), 7·11 (2 H, d), 7·62 (4 H, dd), 8·20 (2 H, d). ^{13}C NMR ($CDCl_3$): δ 11·93, 14·66, 17·21, 17·95, 23·23, 26·34, 26·84, 29·84, 32·21, 35·86, 68·78, 72·73, 74·57, 75·51, 115·60 (C 2), 115·88 (2 C), 123·05 (2 C), 127·37 (2 C), 128·22, 128·99 (2 C), 131·27 (2 C), 132·62, 145·14, 146·50, 157·31, 160·18, 166·10. MS: 518 (M^+), 281, 197. Elemental anal. for $C_{33}H_{42}O_5$: calcd C: 76·45, H: 8·11; found C: 76·74, H: 8·14.

4.5. *4-{2(S)—[2(S)-methylbutyloxy]propoxy}phenyl 4-(4-heptyloxyphenyl)benzoate* (**10**)

$[\alpha]_D^{25} = -10{\cdot}6°$ (C = 1·0, $CHCl_3$). FTIR (KBr): 2950, 1729, 1603, 1508, 1290, 1075, 826 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0·86 (9 H, m), 1·20 (1 H, m), 1·25 (3 H, d), 1·50 (10 H, m),

1·81 (2 H, m), 3·36 (2 H, m), 3·8 (2 H, m), 4·0 (3 H, m), 6·95 (4 H, m), 7·10 (2 H, d), 7·62 (4 H, dd), 8·20 (2 H, d). ^{13}C NMR ($CDCl_3$): δ 11·88, 14·66, 17·15, 17·90, 23·18, 26·58, 26·78, 29·63, 29·82, 32·35, 35·80, 68·70, 72·65, 74·50, 75·44, 115·52 (2 C), 115·81 (2 C), 127·08 (2 C), 128·15, 128·91 (2 C), 131·21 (2 C), 132·52, 145·08, 146·41, 157·25, 160·12, 166·01. MS: 532 (M^+), 295, 197, 71. Elemental anal. for $C_{34}H_{44}O_5$: calcd C: 76·69, H: 8·27, found C: 76·68, H: 8·37.

4.6. *4-{2(S)-[2(S)-methylbutyloxy]propoxy}phenyl 4-(4-octyloxyphenyl)benzoate* (**11**)

$[\alpha]_D^{25} = -5·6°$ (C = 0·71, $CHCl_3$). FTIR (KBr): 2954, 2856, 1730, 1617, 1508, 1291, 1195, 1078 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0·88 (9 H, m), 1·15 (1 H, m), 1·30 (3 H, m), 1·50 (10 H, m), 1·60 (2 H, m), 1·80 (2 H, m), 3·36 (2 H, m), 3·80 (2 H, m), 3·95 3 H, m), 6·96 (4 H, m), 7·12 (2 H, d), 7·62 (4 H, dd) 8·20 (2 H, d). ^{13}C NMR ($CDCl_3$): δ 11·91, 14·71, 17·18, 17·93, 23·27, 26·65, 26·81, 29·85 (2 C), 29·96, 32·42, 35·84, 68·76, 72·68, 74·53, 75·50, 115·56 (2 C), 115·85 (2 C), 123·03 (2 C), 127·15 (2 C), 128·18, 128·97 (2 C), 131·26 (2 C), 132·59, 145·09, 146·48, 157·28, 160·14, 166·01. MS: 546 (M^+), 309, 197, 71. Elemental anal. for $C_{35}H_{46}O_5$: calcd C: 76·92, H: 8·42; found C: 76·54, H: 8·48.

4.7. *4-{2(S)-[2(S)-methylbutyloxy]propoxy}phenyl 4-(4-nonyloxyphenyl)benzoate* (**12**)

$[\alpha]_D^{25} = -9·9°$ (C = 0·91, $CHCl_3$). FTIR (KBr): 2958, 2853, 1729, 1617, 1507, 1290, 1195, 1078 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0·90 (9 H, m), 1·15 (1 H, m), 1·28 (3 H, d), 1·45 (12 H, m), 1·65 (2 H, m), 1·80 (2 H, m), 3·36 (2 H, m), 3·81 (2 H, m), 3·99 (3 H, m), 6·98 (4 H, m), 7·14 (2 H, d), 7·64 (4 H, dd), 8·23 (2 H, d). ^{13}C NMR ($CDCl_3$): δ 11·97, 14·77, 17·25, 17·99, 23·33, 26·71, 26·88, 29·92, (2 C), 30·07, 30·20, 32·54, 35·91, 68·82, 72·77, 74·60, 75·55, 115·64 (2 C), 115·92 (2 C), 123·09 (2 C), 127·20 (2 C), 128·26, 129·02 (2 C), 131·31 (2 C), 132·65, 145·18, 146·54, 157·35, 160·22, 166·14. MS: 560 (M^+), 323, 197, 71. Elemental anal. for $C_{36}H_{48}O_5$: calcd C: 77·14, H: 8·57; found C: 77·15, H: 8·62.

4.8. *4-{2(S)−[2(S)-methylbutyloxy]propoxy}phenyl 4-(4-decyloxyphenyl)benzoate* (**13**)

$[\alpha]_D^{25} = -6·3°$ (C = 0·96, $CHCl_3$). FTIR (KBr): 2924, 1729, 1605, 1505, 1251, 1088, 813 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0·88 (9 H, m), 1·15 (1 H, m), 1·25 (3 H, d), 1·40 (14 H, m), 1·60 (2 H, m), 1·80 (2 H, m), 3·36 (2 H, m), 3·80 (2 H, m), 3·95 (3 H, m), 6·96 (4 H, m), 7·12 (2 H, d), 7·62 (4 H, dd), 8·21 (2 H, d). ^{13}C NMR ($CDCl_3$): δ 11·89, 14·71, 17·17, 17·92, 23·27, 26·63, 26·80, 29·84, 29·91, 29·99 (2 C), 30·16, 32·49, 35·83, 68·74, 72·67, 74·52, 75·47, 115·56 (2 C), 115·83 (2 C), 123·01 (2 C), 127·12 (2 C), 128·17, 128·94 (2 C), 131·24 (2 C), 132·56, 145·09, 146·44, 157·27, 160·14, 166·06. MS: 574 (M^+), 337, 197, 71. Elemental anal. for $C_{37}H_{50}O_5$: calcd C: 77·35, H: 8·71; found C: 77·14, H: 8·79.

4.9. *4-{2(S(−[2(S)-methylbutyloxy]propoxy}phenyl 4-(4-dodecyloxyphenyl)benzoate* (**14**)

$[\alpha]_D^{25} = -8·7°$ (C = 1·03, $CHCl_3$). FTIR (KBr): 2924, 1729, 1604, 1509, 1295, 1197, 1084, 831 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0·88 (9 H, m), 1·15 (1 H, m), 1·25 (3 H, d), 1·45 (18 H, m), 1·60 (2 H, m), 1·80 (2 H, m), 3·36 (2 H, m), 3·79 (2 H, m), 3·96 (3 H, m), 6·96 (4 H, m), 7·12 (2 H, d), 7·62 (4 H, dd), 8·21 (2 H, d). ^{13}C NMR ($CDCl_3$): δ 11·89, 14·71, 17·71, 17·91, 23·28, 26·63, 26·80, 29·84, 29·94 (3 C), 30·19 (3 C), 32·51, 35·82, 68·74, 72·67, 74·52, 75·47, 115·56 (2 C), 115·84 (2 C), 123·02 (2 C), 127·12 (2 C), 128·17, 128·94 (2 C), 131·24 (2 C), 132·56, 145·09, 146·45, 157·27, 160·14, 166·08. MS: 602 (M^+), 365, 197, 71. Elemental anal. for $C_{39}H_{54}O_5$: calcd C: 77·74, H: 8·97; found C: 77·55, H: 8·97.

This work was generously supported by the Ministry of Economic Affairs, the Republic of China.

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