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A comparison of ferroelectric liquid crystals containing diastereomeric propionic acids derived from natural ethyl lactate

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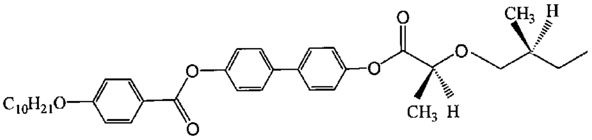
Two diastereomeric carboxylic acids, 2(*S*)-[2(*R*)-methylhexyloxy]propionic acid and 2(*S*)-[2(*S*)-methylhexyloxy]propionic acid, were prepared from ethyl (*S*)-lactate and (*R*)-1-iodo-2-methylhexane or (*S*)-1-iodo-2-methylhexane in the presence of Ag_2O. From these acids two liquid crystals, **2** and **3**, whose configurations are (*S*, *R*) and (*S*, *S*) were synthesized and their liquid crystal properties investigated. Although both LCs have the same phase sequence Cr–SmC*–N*–I as well as a wide SmC* phase range, the influence of the relative stereochemistry on their physical properties is clear. The liquid crystal with (*S*, *S*)-configuration possesses better properties: lower SmC* phase transition temperature, wider SmC* phase range and higher $\mathbf{P}_s$ value. The $\mathbf{P}_s$ value difference between the ferroelectric LCs **2** and **3** (97 and 131 nC cm^{-2}, respectively, at $T_c - T = 10°C$) is unexpectedly large. The consideration, alone, of a zigzag conformation at the chiral molecular part of **2** and **3** is insufficient to explain such a difference.

1. Introduction

Chiral liquid crystals have attracted great attention due to their novel properties such as thermochromism [1], ferroelectricity [2] and antiferroelectricity [3]. Therefore, the absolute and relative configurations of chiral molecules are important in the design and synthesis of new chiral liquid crystals with improved properties [4, 5]. We have recently used a molecule with two chiral centres, 2(*S*)-[2(*S*)-methylbutoxy]propionic acid, as a building block for the preparation of ferroelectric liquid crystals (FLCs) [6, 7]. It was shown that the spontaneous polarization of these FLCs could be increased enormously [8]. Although the two chiral methyl groups in those FLC molecules, for instance FLC **1**, are relatively far away from each other, separated by an oxygen atom and a methylene group, they seem to work in a coherent way to induce a larger spontaneous polarization. It is known that the influence of a chiral methyl group on the spontaneous polarization will be decreased greatly when it moves further away from the core [9–11]. However, the second (*S*)-methyl group in these FLCs, even far away from the core, has an unexpected and encouraging effect. To understand the effect clearly, two chiral liquid crystals with (*S*, *R*)- and (*S*, *S*)-configuration, as shown in structures **2** and **3**, were synthesized and their phase behaviours and spontaneous polarization were studied and compared.



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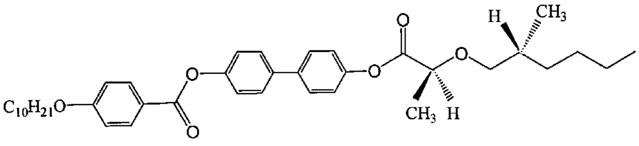

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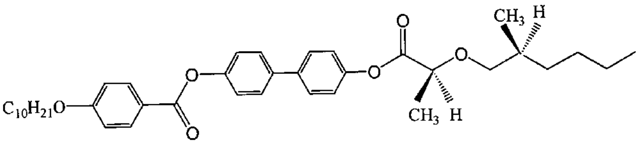

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2. Experimental

2.1. *Characterization*

Infrared and NMR spectra were recorded on a Nicolet 550 FTIR and Brucker AC-300 spectrometer, respectively. Elemental analyses were made by a Heraeus CHN-O-RAPID combustion apparatus. Mass spectra were recorded on a JMS-D100 instrument. Specific rotation was measured with a Horiba SEPA-300 polarimeter. Transition temperatures and textures of liquid crystal phases were determined by a Perkin-Elmer DSC-6 differential scanning calorimeter, as well as with an Olympus BX 50 polarizing microscope in conjunction with an Instec HS 400 heating stage. Spontaneous polarizations were measured by the triangular wave method [12]. Cells having 2 μm gap and 0.16 cm^2 active area were used.

2.2. *Synthesis*

Only the syntheses of compounds having the (*S*, *R*)-configuration are described here. The procedures used for the preparation of the corresponding (*S*, *S*)-stereoisomers were analogous to those for the (*S*, *R*)-stereoisomers. Commercially available chemical reagents were used directly without further purification. Solvents for chromatography and recrystallization were distilled before use. Silica gel 60 from Merck was used as packing material for flash chromatography.

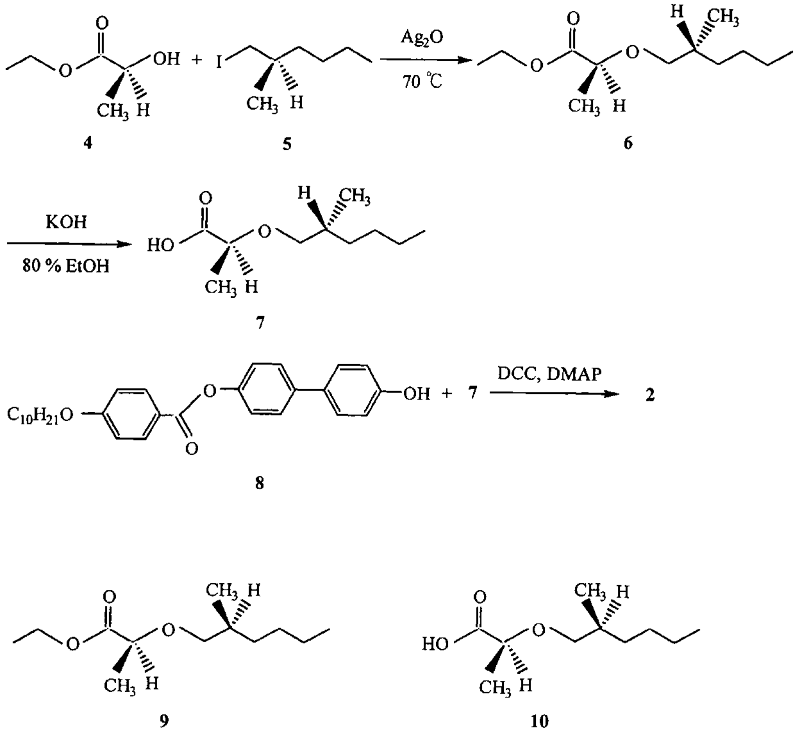
The synthesis of new chiral compounds and FLCs having an (*S*, *R*)-configuration is shown in the scheme. The chiral starting material, (*R*)-1-iodo-2-methylhexane (**5**), was synthesized from racemic 2-methylhexanoic acid by optical resolution [13], reduction [14] and iodination [15]. The alkaloid cinchonidine was used as the resolving agent for (*R*)-2-methylhexanoic acid, while quinine was used for (*S*)-2-methylhexanoic acid. The new chiral propionic ester **6** was prepared by the esterification of natural ethyl lactate (**4**) with **5** in the presence of Ag_2O.

After saponification of **6** the new chiral propionic acid **7** was formed. The esterification of **7** with the 4,4′-biphenol derivative **8** gave the target liquid crystal compound **2**. The corresponding diastereomers having (*S*, *R*)-configuration, **9**, **10** and **3**, were synthesized by the same procedures as those for **6**, **7** and **2**.

The configuration of the synthesized diastereomers can be easily identified by ^{1}H NMR. The chemical shift of the methylene group between the oxygen atom of the first chiral centre and the second chiral centre is useful for differentiating the (*S*, *R*)-stereoisomers from the corresponding (*S*, *S*)-stereoisomers. Those methylene groups all have AB patterns. The AB pattern of the (*S*, *R*)-stereoisomer is positioned between that of the corresponding (*S*, *S*)-stereoisomer. For comparison the chemical shift of the methylene group and the specific rotation of the diastereomers **2**, **3**, **6**, **7**, **9** and **10** are summarized in table 1.

2.2.1. *Ethyl 2(S)-[2(R)-methylhexyloxy]propionate (6)*

To a mixture of 2.24 g (19.0 mmol) of ethyl (*S*)-lactate (**4**) and 6.00 g (26.5 mmol) of (*R*)-1-iodo-2-methylhexane



Scheme.

Table 1. Chemical shifts and specific rotations of compounds **2**, **3**, **6**, **7**, **9** and **10**.

Compound	Chemical shift/ppm $-(CH_3)$*$CH-O-C\underline{H}_2-$*$CH(CH_3)-$	$[\alpha]_D^{28}(CHCl_3)$/°
6 (ester)	3.17, 3.29	− 50
9 (ester)	3.12, 3.42	− 49
7 (acid)	3.26, 3.34	− 30
10 (acid)	3.13, 3.43	− 24
2 (FLC)	3.35, 3.46	− 22
3 (FLC)	3.23, 3.58	− 29

(**5**) [13–15], 6.54 g (28.2 mmol) of silver oxide was added and the mixture heated at 70°C for 18 h. The product was extracted with diethyl ether (5 × 30 ml), and the ether phase washed with 5% aqueous KOH (5 × 30 ml) and then with brine (5 × 30 ml). The organic phase was collected and dried over Na_2SO_4. Filtration and removal of solvent in a rotary evaporator gave crude product which was purified by flash chromatography (pentane/diethyl ether, 10/1), affording 2.31 g (56%) of ester **6** as a colourless liquid. IR (neat) 2962, 1742, 1472, 1375, 1273, 1135 cm^{-1}. ^1H NMR ($CDCl_3$) 0.87 ~ 1.37 (peaks overlapped, 18H), 1.68 (m, 1H, $-OCH_2-C\underline{H}(CH_3)-CH_2-$), 3.17 (d (AB) × d, 1H, $J = 8.6$, 6.3 Hz, $-O-(C{=}O)-CH(CH_3)-OC\underline{H}_2-$), 3.29 (d (AB) × d, 1H, $J = 8.6$, 6.8 Hz, $-O-(C{=}O)-CH(CH_3)-OC\underline{H}_2-$), 3.87 (q, 1H, $J = 6.8$ Hz, $-O-(C{=}O)-C\underline{H}(CH_3)-O-$), 4.16 (q, 2H, $J = 6.9$ Hz, $CH_3-C\underline{H}_2-O-(C{=}O)-$). ^{13}C NMR ($CDCl_3$) 14.04, 16.94, 18.62, 22.31, 22.93, 29.12, 33.23, 34.13, 60.66, 75.33, 75.88, 173.57. MS (FAB) *m/z* (relative intensity): 217 ($M^+ + 1$, 24.4); $[\alpha]_D^{28} = -49.5°$ ($CHCl_3$, $c = 1.01$).

2.2.2. *2(S)-[2(R)-Methylhexyloxy]propionic acid (7)*

To a solution of 2.30 g (10.6 mmol) of **6** in 15 ml of ethanol was added to a solution of 1.40 g (25.0 mmol) of KOH in 10 ml of 80% ethanol. After heating under reflux for 2 h the ethanol was removed. The residue was acidified with 1.0M HCl at 0°C. After extraction with CH_2Cl_2 (4 × 50 ml), the organic phase was washed with brine (4 × 50 ml) and dried over Na_2SO_4. Filtration and removal of solvent gave 1.95 g (98%) of acid **7** as a colourless viscous oil. IR (neat) 3360, 1740, 1450, 1365, 1273, 1060 cm^{-1}. ^1H NMR ($CDCl_3$) 0.88 ~ 1.43 (peaks overlapped, 15 H), 1.70 (m, 1H, $-OCH_2-C\underline{H}(CH_3)-CH_2-$), 3.26 (d, (AB) × d, 1H, $J = 8.7$, 6.3 Hz, $-O-(C{=}O)-CH(CH_3)-OC\underline{H}_2-$), 3.34 (d, (AB) × d, 1H, $J = 8.7$, 6.8 Hz, $-O-(C{=}O)-CH(CH_3)-OC\underline{H}_2-$), 3.95 (q, 1H, $J = 6.6$ Hz, $-OC\underline{H}(CH_3)-COOH$). ^{13}C NMR ($CDCl_3$) 14.04, 16.90, 18.11, 22.89, 29.07, 33.13, 33.38, 74.73, 76.04, 177.65. MS (FAB) *m/z* (relative intensity): 189 ($M^+ + 1$, 17.5); $[\alpha]_D^{28} = -29.5°$ ($CHCl_3$, $c = 1.01$).

2.2.3. *4-{2(S)-[2(R)-Methylhexyloxy]propionyloxy}-biphenyl 4-n-decyloxybenzoate (2)*

A solution of 223.0 mg (0.50 mmol) of 4-(4′-hydroxy)-biphenyl 4-*n*-decyloxybenzoate (**8**), 94.0 mg (0.50 mmol) of **7**, 61.1 mg (0.50 mmol) of 4-(*N*,*N*-dimethylamino)-pyridine, 151.7 mg (1.50 mmol) of triethylamine and 113.3 mg (0.55 mmol) of dicyclohexylacarbodiimide in 4 ml of CH_2Cl_2 was stirred at room temperature for 18 h. The precipitate was filtered off and washed with 10 ml of CH_2Cl_2. The combined organic phase was washed with 0.1M HCl (3 × 5 ml) and H_2O (3 × 5 ml), then dried over Na_2SO_4. Filtration, removal of solvent, purification by flash chromatography (SiO_2, hexane/ethylacetate/CH_2Cl_2, 6/1/1), and recrystallization from hexane gave the product as a white solid in 42% yield. IR (KBr) 2920, 2849, 1768, 1720, 1616, 1496, 1168 cm^{-1}. ^1H NMR ($CDCl_3$) 0.84 ~ 1.83 (peaks overlapped, 35 H), 3.35 (d (AB) × d, 1H, $J = 7.0$, 1.7 Hz, $-O-(C{=}O)-CH(CH_3(-O-C\underline{H}_2-CH(CH_3)-)$, 3.46 (d (AB) × d, 1H, $J = 7.0$, 1.5 Hz, $-O-(C{=}O)-CH(CH_3)-O-C\underline{H}_2-CH(CH_3)-$), 4.03 (t, 2H, $J = 6.6$ Hz, $-C\underline{H}_2-O-Ar$), 4.16 (q, 1H, $J = 6.6$ Hz, $-O-(C{=}O)-C\underline{H}(CH_3)-O-$), 6.95 (d, 2H, $J = 8.7$ Hz, $Ar-\underline{H}$), 7.16 (d, 2H, $J = 8.4$ Hz, $Ar-\underline{H}$), 7.25 (d, 2H, $J = 9.0$ Hz, $Ar-\underline{H}$), 7.58 (d, 2H, $J = 7.2$ Hz, $Ar-\underline{H}$), 7.59 (d, 2H, $J = 6$ Hz, $Ar-\underline{H}$), 8.13 (d, 2H, $J = 8.7$ Hz, $Ar-\underline{H}$). ^{13}C NMR ($CDCl_3$) 14.1, 17.0, 18.7, 22.7, 22.9, 25.9, 29.1, 29.3, 29.6, 31.9, 33.2, 33.5, 68.3, 75.1, 76.2, 114.3, 121.4, 121.7, 122.1, 128.1, 128.2, 132.3, 137.9, 138.3, 149.9, 150.6, 163.6, 165.0, 172.1; $[\alpha]_D^{25} = -23.4°$ ($CHCl_3$, $c = 0.93$). Elemental analysis for $C_{39}H_{52}O_6$: calc. C 75.94, H 8.50; found C 75.90, H 8.64%.

3. Liquid crystal properties

The stereochemistry of the chiral molecular part of the liquid crystals was modified in order to study the influence of the configuration at the second chiral centre on the liquid crystal properties. Two diastereomeric liquid crystals **2** and **3** were synthesized and investigated. The latter has (*S*, *S*)-configuration, the former has (*S*, *R*)-configuration. Their liquid crystal phases and phase transition temperatures were identified by differential

Table 2. Physical properties of the FLCs **1**, **2** and **3**.

	Phase transition/°C								
Compound	Cr		SmC*		N*		I		$\mathbf{P}_s$/nC cm^{-2}
2	•	80	•	121	•	123	•		97
3	•	73	•	119	•	121	•		131
1	•	83	•	129	•	134	•		118

scanning calorimetry and polarizing microscopy. The spontaneous polarization was measured at $T_c - T = 10°C$ by the triangular wave method, using a cell with a 2 µm gap and 0.16 cm^2 active area. An a.c. field of 20 V and 100 Hz was applied to the system. The results are summarized in table 2. The corresponding properties of FLC **1** [6, 8] is included in the table for comparison.

It is the phase transition temperature and the phase range, not the phase sequence, which are affected by the relative stereochemistry and the alkyl chain length of the chiral molecular part. Both liquid crystals **2** and **3** exhibit the same phase sequence, Cr–SmC*–N*–I, as **1**. But the phase transition temperatures **2** and **3** are lower than those of **1**. The SmC* phase transition temperature of **3** is the lowest one among these three FLCs. They all have a wide SmC* phase temperature range, between 41 and 46°C. In comparison with **1**, both liquid crystals **2** and **3** have not only lower N* phase transition temperatures but narrower N* phase ranges.

The spontaneous polarization of **3** is larger than that of **1**, 131 and 118 nC cm^{-2}, respectively. The alkyl chain of **3** on the external side of the second chiral centre is two carbon atoms longer than that of **1**. In the situation where the alkyl chain is longer, the rotation of the chiral molecular part is more hindered with respect to the rest of the liquid crystal molecule. This in turn could increase the spontaneous polarization. Another study [16] has reported similar results. An enormous variation of $\mathbf{P}_s$ value from 131 nC cm^{-2} for **3** to 97 nC cm^{-2} for **2** is observed when the relative stereochemistry of the FLCs is changed from (*S*, *S*)-configuration to (*S*, *R*)-configuration. The known results [9–11] indicate that the contribution of a moiety at a chiral centre to the spontaneous polarization of FLCs will be very small when it is moved further away from the core. This is not the case for **2** and **3**. Although the second chiral centre of **2** and **3** is far way from the biphenyl ring, it has a remarkable effect on the variation of the spontaneous polarization. The dipole moment of a methyl group, compared with that of a carbonyl group and an ether linkage, is very small. For this reason the contribution of the methyl groups at the second chiral centre to the spontaneous polarization of **2** and **3** is negligible. In other words, the sole consideration of a zigzag conformation at the chiral molecular part of **2** and **3** is insufficient to explain their spontaneous polarization difference. Different modification of the conformation and, therefore, different intermolecular interaction between **2** and **3** due to the presence of the second chiral centre is considered to be a plausible reason for such a variation.

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