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Mesogenic properties of chiral compounds derived from 2(S)-[2(S)-ethylhexyloxy] propionic acid and its (S, R)-diastereomer

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Mesogenic properties of chiral compounds derived from 2(*S*)-[2(*S*)-ethylhexyloxy]propionic acid and its (*S*, *R*)-diastereomer

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Two acids, 2(*S*)-[2(*S*)-ethylhexyloxy]propionic acid and 2(*S*)-[2(*R*)-ethylhexyloxy]propionic acid, were used as the chiral building block for the preparation of four liquid crystals **5**, **6**, **7** and **8**. The diastereomers of the biphenyl ring system, **5** and **6**, possess the phase sequence I–N*–SmC*–Cr1–Cr2, while the diastereomers of the naphthalene ring system, **7** and **8**, exhibit the sequence I–SmA–SmC*–Cr. The temperature ranges of the SmC* phase for **5** and **6** are wider than those for **7** and **8**; the phase transition temperatures of the SmC* phase for **7** and **8** are lower than those for **5** and **6**. In the case of the diastereomers of naphthalene ring system, the larger the size of the lateral substituent at the second chiral centre, i.e. ethyl or methyl group, the wider the temperature range of the SmC* phase.

1. Introduction

Chiral liquid crystals (LCs) have long been of great interest to chemists, and many efforts have been made to correlate their stereochemistry with their mesogenic and electrooptical properties such as ferroelectric polarization [1–6] and helical twisting power [7]. We have recently prepared two series of diastereomeric compounds **1**, **2**, **3** and **4**, all of which are ferroelectric liquid crystals. Results indicate that the conformation change induced by the second chiral centre, and the core molecule connected directly to chiral moiety, can have a significant effect on ferroelectricity and LC phases [8, 9]. It is known that the size of substituents can induce the conformation change of stereoisomers; this will then influence their physical properties. In order to study the substituent effect at the second chiral centre, four chiral liquid crystals **5**, **6**, **7** and **8**, having an ethyl group instead of a methyl group at the second chiral centre, were synthesized. Their mesogenic properties have been studied and the substituent effect is discussed below. The structures of compounds **1**–**8** are shown in figure 1.

2. Experimental

2.1. *Characterization*

Infrared and NMR spectra were recorded on Nicolet 550 FTIR and Brucker AMX-400 spectrometers, respectively. Mass spectra were observed on a JMS-D100 instrument. Elemental analyses were made using a Heraeus CHN-O-RAPID combustion apparatus. Specific rotation was measured with a Horiba SEPA-300 polarimeter. Transition temperatures and textures of liquid crystal phases were determined using a Perkin-Elmer DSC-6 differential scanning calorimeter, and an Olympus BX50 polarizing microscope in conjunction with an Instec HS 400 heating stage.

2.2. *Synthesis*

Commercially available chemical reagents were used directly without further purification. Solvents for chromatography and recrystallization were distilled before use. Chromatographic purifications were performed using flash chromatography over Merck silica gel 60. Only the reaction procedures for the compounds having the (*S*, *S*)-configuration are described.

The synthesis of the new chiral compounds having the (*S*, *S*)-configuration is shown in figure 2. The chiral starting material, (*S*)-1-iodo-2-ethylhexane **10**, was synthesized from racemic 2-ethylhexanoic acid by optical resolution [10], reduction [11], tosylation, and iodination. The amine (*R*)-1-phenylethylamine was used as the resolving agent for (*S*)-2-ethylhexanoic acid. The new chiral propionic ester **11** was synthesized by the esterification of natural ethyl acetate **9** with **10** in the presence of Ag_2O. After saponification of **11** the new chiral propionic acid **12** was formed. The esterification of **5**

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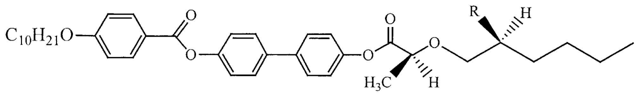
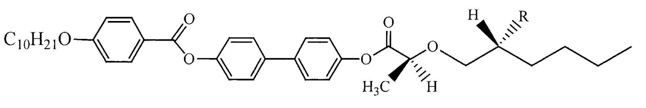
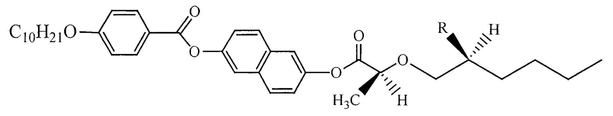


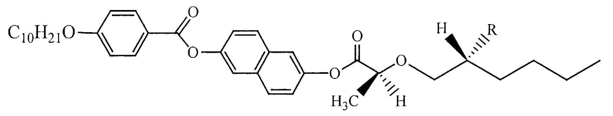
1 : R= CH_3 ; **5** : R= C_2H_5



2 : R= CH_3 ; **6** : R= C_2H_5



3 : R= CH_3 ; **7** : R= C_2H_5



4 : R= CH_3 ; **8** : R= C_2H_5

Figure 1. Structure of compounds **1**–**8**.

with the 4,4′-biphenol derivative **13** or 2,6-dihydroxynaphthalene derivative **14** gave the corresponding liquid crystal compounds **5** or **7**.

The configuration of these diastereomers can be easily identified by the chemical shift of the methylene group between the oxygen atom of the first chiral centre and the second chiral centre. The protons at these methylene groups are diastereotopic and the splitting pattern for the (*S*, *R*)-diastereomer is positioned between that of the corresponding (*S*, *S*)-diastereomer.

2.2.1. *Ethyl 2(S)-[2(S)-ethylhexyloxy]propionate (11)*

To a mixture of 3.54 g (30 mmol) of ethyl (*S*)-lactate **9** and 3.48 g (14.50 mmol) of (*S*)-1-iodo-2-ethylhexane **10** was added 3.47 g (15 mmol) of silver(I) oxide, and the mixture was heated at 75–80°C for 24 h. The reaction mixture was washed with diethyl ether (30 ml) and the ether phase washed with 5% aqueous KOH (4 × 30 ml) and then with H_2O (4 × 30 ml). The organic phase was dried over $MgSO_4$. Filtration and removal of solvent in a rotary evaporator gave the crude product which was purified by flash chromatography (SiO_2, ethyl acetate/hexane, 1/15) affording 1.00 g of ester **11** as a colourless liquid in 30% yield. $[\alpha]_D^{25} = -40.8°$ (MeOH, $c = 1.05$). IR (neat) 2967, 1756, 1466, 1381, 1269, 1137, 1072 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.79–0.84 (m, 6H, $-O-CH_2-CH(CH_2C\underline{H}_3)-CH_2CH_2CH_2C\underline{H}_3$), 1.19–1.50 (m, 15H, $C\underline{H}_3-CH_2-O-(C{=}O)-CH(C\underline{H}_3)-O-CH_2-C\underline{H}(C\underline{H}_2CH_3)-C\underline{H}_2-C\underline{H}_2-C\underline{H}_2-CH_3$), 3.15 (d × d, 1H, $J = 5.9$, 8.8 Hz, $-CH(CH_3)-O-C\underline{H}_2-CH(CH_2CH_3)-$), 3.45 (d × d, 1H, $J = 5.4$, 8.9 Hz, $-CH(CH_3)-O-C\underline{H}_2-CH(CH_2CH_3)-$), 3.85 (q, 1H, $J = 6.8$ Hz, $-(C{=}O)-C\underline{H}(CH_3)-O-$), 4.15 (m, 2H, $-O-C\underline{H}_2-CH_3$). ^{13}C NMR ($CDCl_3$) δ 10.83, 13.91, 14.06, 18.46, 22.90, 23.62, 28.91, 30.27, 39.61, 60.44, 72.94, 75.14, 173.41. MS (FAB) *m/z* (relative intensity): 231 ($M^+ + 1$, 10.4), 113 (100). HRMS: calc. $M = 230.1882$, found = 230.1882. Elemental analysis for $C_{13}H_{26}O_3$: calc. C 67.79, H 11.38; found C 67.33, H 11.38%.

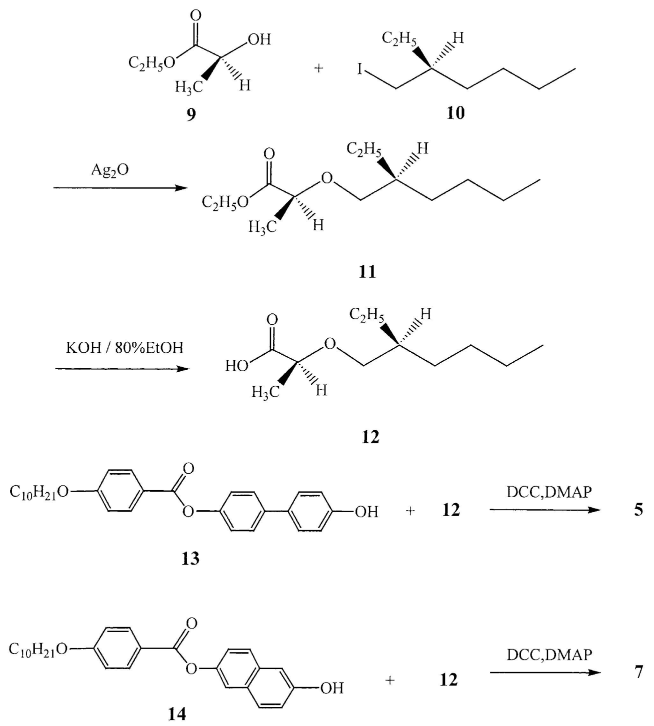


Figure 2. Synthesis of compounds **5** and **7**.

2.2.2. *2(S)-[2(S)-Ethylhexyloxy]propionic acid (12)*

A solution of 1.0 g (4.35 mmol) of **11** in 10 ml of ethanol was added to a solution of 0.82 g (14.85 mmol) of KOH in 10 ml of 80% ethanol and the mixture heated at 95–100°C for 1.5 h. Ethanol was removed and the residue acidified with 1.0M HCl at 0°C. After extraction with CH_2Cl_2 (4 × 20 ml) the organic phase was washed with H_2O (3 × 20 ml) and dried over $MgSO_4$. Filtration and removal of solvent gave 0.53 g of acid **5** as a colourless viscous oil in 60% yield. $[\alpha]_D^{25} = -36.1°$ (MeOH, $c = 1.02$); IR (neat): 3165, 2993, 1723, 1249, 1137 cm^{-1}.

^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.80–0.93 (m, 6H, $\mathrm{-O-CH_2-CH(CH_2C\underline{H}_3)-CH_2CH_2CH_2C\underline{H}_3}$), 1.15–1.70 (m, 12H, $\mathrm{-CH(C\underline{H}_3)-O-CH_2-C\underline{H}(C\underline{H}_2CH_3)-C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3}$), 3.30 (d × d, 1H, $J = 6.2$, 9.0 Hz, $\mathrm{-CH(CH_3)-O-C\underline{H}_2-CH(CH_2CH_3)-}$), 3.49 (d × d, 1H, $J = 5.6$, 9.2 Hz, $\mathrm{-CH(CH_3)-O-C\underline{H}_2-CH(CH_2CH_3)-}$), 3.95 (q, 1H, $J = 7.0$ Hz, $\mathrm{-(C{=}O)-C\underline{H}(CH_3)-O-}$), 9.57 (broad s, 1H, $\mathrm{-COOH}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 10.89, 14.01, 18.18, 22.97, 23.63, 28.93, 30.23, 39.60, 73.24, 74.75, 178.37. MS (EI) *m/z* (relative intensity): 202 ($\mathrm{M^+}$, 7.9), 57 (100). HRMS: calc. $M = 202.1569$, found $M = 202.1568$. Elemental analysis for $\mathrm{C_{11}H_{22}O_3}$: calc. C 65.31, H 10.96; found C 65.53, H 11.05%.

2.2.3. *4-{2-(S)-[2-(S)-Ethylhexyloxy]propionyloxy} biphenyl 4-n-decyloxybenzoate (**5**)*

A solution of 223.0 mg (0.50 mmol) of 4′-hydroxybiphenyl 4-*n*-decyloxybenzoate **13**, 101.1 mg (0.50 mmol) of **12**, 61.1 mg (0.50 mmol) of 4-(*N*,*N*-dimethylamino)pyridine, 158.5 mg (1.60 mmol) of triethylamine and 120.4 mg (0.58 mmol) of dicyclohexyl carbodiimide in 3 ml of $\mathrm{CH_2Cl_2}$ was stirred at room temperature for 24 h. The precipitate was filtered off and washed with 40 ml of $\mathrm{CH_2Cl_2}$. The organic phase was washed with 10 ml of 0.1M HCl and 10 ml of $\mathrm{H_2O}$. Removal of solvent, purification by flash chromatography ($\mathrm{SiO_2}$, ethyl acetate/hexane, 1/14), and recrystallization from hexane and ethyl acetate gave 122 mg of the product as a white solid in 39% yield. $[\alpha]_D^{25} = -23.7°$ ($\mathrm{CHCl_3}$, $c = 1.032$). IR (KBr) 2940, 2842, 1776, 1736, 1618, 1499, 1473, 1328, 1275, 1210, 1170, 1124, 1085 $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.85–0.95 (m, 9H, $\mathrm{C\underline{H}_3(CH_2)_7CH_2CH_2O-}$, $\mathrm{-OCH_2CH\text{-}(CH_2C\underline{H}_3)CH_2CH_2-CH_2C\underline{H}_3}$), 1.20–1.62 (m, 26H, $\mathrm{CH_3(C\underline{H}_2)_7CH_2CH_2O-}$, $\mathrm{-OCH_2C\underline{H}-(C\underline{H}_2CH_3)C\underline{H}_2\text{-}C\underline{H}_2C\underline{H}_2CH_3}$, $\mathrm{-O-(C{=}O)-CH(C\underline{H}_3)-O-}$), 1.80–1.87 (m, 2H, $\mathrm{CH_3(CH_2)_7C\underline{H}_2CH_2O-}$), 3.36 (d × d, 1H, $J =$ 6.2, 8.6 Hz, $\mathrm{CH(CH_3)-O-C\underline{H}_2-CH(CH_3)-}$), 3.64 (d × d, 1H, $J = 5.6$, 8.8 Hz, $\mathrm{CH(CH_3)-O-C\underline{H}_2-CH(CH_3)-}$), 4.05 (t, 2H, $J = 6.6$ Hz, $\mathrm{CH_3(CH_2)_8C\underline{H}_2O-}$), 4.18 (q, 1H, $J = 6.9$ Hz, $\mathrm{-O-(C{=}O)-C\underline{H}(CH_3)O-}$), 6.90 (d, 2H, $J =$ 8.8 Hz, $\mathrm{Ar-\underline{H}}$), 7.19 (d, 2H, $J = 8.8$ Hz, $\mathrm{Ar-\underline{H}}$), 7.29 (d, 2H, $J = 8.8$ Hz, $\mathrm{Ar-\underline{H}}$), 7.59 (d, 2H, $J = 2.4$ Hz, $\mathrm{Ar-\underline{H}}$), 7.61 (d, 2H, $J = 2.0$ Hz, $\mathrm{Ar-\underline{H}}$), 8.16 (d, 2H, $J = 8.8$ Hz, $\mathrm{Ar-\underline{H}}$). ^{13}C NMR ($\mathrm{CDCl_3}$): 11.06, 14.09, 18.67, 22.66, 23.04, 23.75, 25.95, 29.04, 29.06, 29.32, 29.53, 29.57, 30.40, 31.88, 39.78, 68.31, 73.39, 75.26, 114.29, 121.39, 121.66, 122.14, 128.13, 128.17, 132.29, 137.88, 138.34, 149.91, 150.58, 163.57, 164.96, 172.13. HRMS: calc. $M = 631.3999$, found $M = 631.3995$. Elemental analysis for $\mathrm{C_{40}H_{54}O_6}$: calc. C 76.16, H 8.63; found C 76.19, H 8.75%.

2.2.4. *6-{2-(S)-[2-(S)-Ethylhexyloxy]propionyloxy}-2-naphthyl 4-n-decyloxybenzoate (7)*

A solution of 219.9 mg (0.50 mmol) of 6-hydroxy-2-naphthyl 4-*n*-decyloxybenzoate **14**, 101.1 mg (0.50 mmol) of **12**, 61.1 mg (0.50 mmol) of 4-(*N*,*N*-dimethylamino)pyridine, 158.5 mg (1.60 mmol) of triethylamine and 120.4 mg (0.58 mmol) of dicyclohexylacarbodiimide in 3 ml of $\mathrm{CH_2Cl_2}$ was stirred at room temperature for 24 h. The precipitate was filtered off and washed with 40 ml of $\mathrm{CH_2Cl_2}$. The organic phase was washed with 10 ml of 0.1M HCl and 10 ml of $\mathrm{H_2O}$. A crude product was obtained by flash chromatography ($\mathrm{SiO_2}$, acetone). Purification of the crude product by further flash chromatography ($\mathrm{SiO_2}$, ethyl acetate/hexane, 1/14) gave 56.2 mg of the product as a white solid in 19% yield. $[\alpha]_D^{25} = -25.5°$ ($\mathrm{CHCl_3}$, $c = 0.60$). IR (KBr) 2967, 2855, 1782, 1736, 1611, 1585, 1519, 1473, 1420, 1368, 1269, 1229, 1144, 1071, 1019 $\mathrm{cm^{-1}}$. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.87–0.94 (m, 9H, $\mathrm{C\underline{H}_3(CH_2)_7CH_2CH_2O-}$, $\mathrm{-OCH_2CH(CH_2C\underline{H}_3)\text{-}CH_2CH_2CH_2C\underline{H}_3}$), 1.20–2.0 (m, 28H, $\mathrm{CH_3(C\underline{H}_2)_8CH_2O-}$, $\mathrm{-OCH_2C\underline{H}(C\underline{H}_2CH_3)C\underline{H}_2C\underline{H}_2C\underline{H}_2CH_3}$, $\mathrm{-O-(C{=}O)-CH(C\underline{H}_3)O-}$), 3.38 (d × d, 1H, $J = 6.1$, 8.9 Hz, $\mathrm{CH(CH_3)-O-C\underline{H}_2-CH(CH_3)-}$), 3.66 (d × d, 1H, $J = 5.7$, 8.8 Hz, $\mathrm{CH(CH_3)-O-C\underline{H}_2-CH(CH_3)-}$), 4.05 (t, 2H, $J = 6.6$ Hz, $\mathrm{CH_3(CH_2)_8C\underline{H}_2O-}$), 4.21 (q, 1H, $J = 6.8$ Hz, $\mathrm{-O-(C{=}O)-C\underline{H}(CH_3)O-}$), 7.00 (d × d, 2H, $J = 4.7$, 9.0 Hz, $\mathrm{Ar-\underline{H}}$), 7.26 (d × d, 1H, $J = 2.9$, 8.3 Hz, $\mathrm{Ar-\underline{H}}$), 7.38 (d × d, 1H, $J = 2.2$, 8.8 Hz, $\mathrm{Ar-\underline{H}}$), 7.61 (d, 1H, $J = 2.2$ Hz, $\mathrm{Ar-\underline{H}}$), 7.69 (d, 1H, $J = 2.2$ Hz, $\mathrm{Ar-\underline{H}}$), 7.84 (d, 1H, $J = 4.4$ Hz, $\mathrm{Ar-\underline{H}}$), 7.86 (d, 1H, $J = 4.4$ Hz, $\mathrm{Ar-\underline{H}}$), 8.18 (d × d, 2H, $J = 4.6$, 8.8 Hz, $\mathrm{Ar-\underline{H}}$). ^{13}C NMR ($\mathrm{CDCl_3}$): 11.06, 14.10, 18.69, 22.66, 23.04, 23.76, 25.96, 29.04, 29.07, 29.32, 29.34, 29.53, 29.57, 30.41, 31.88, 39.80, 68.33, 73.44, 75.31, 114.29, 114.32, 118.36, 118.73, 121.37, 121.55, 122.31, 129.01, 129.13, 131.65, 131.85, 132.31, 148.01, 148.73, 163.61, 165.04, 172.20. HRMS: calc. $M = 605.3842$, found $M = 605.3843$. Elemental analysis for $\mathrm{C_{38}H_{52}O_6}$: calc. C 75.46, H 8.67; found C 75.67, H 8.76%.

3. Liquid crystal properties and discussion

The mesogenic phases and phase transition temperatures of chiral compounds **5**–**8** were determined by DSC and texture observation. These data are summarized in the table; the corresponding data for compounds **1**–**4** are included for comparison. The results show that the aromatic ring connected directly to a chiral moiety has a profound influence on the mesogenic properties. While compounds **5** and **6** exhibit the phase sequence I–N*–SmC*–Cr1–Cr2, compounds **7** and **8** possess the sequence I–SmA–SmC*–Cr. The formation of a SmC* phase is obviously unaffected by such a core structure modification. The acid **11** is therefore a useful chiral moiety for the preparation of ferroelectric liquid crystals.

Table. Mesogenic properties of compounds **1**–**8**.

			Phase and phase transition temperatures (°C)										
Compound	*R*	Abs. config.	I		N*		SmA		SmC		Cr1		Cr2
5	C_2H_5	*S*, *S*	•	113	•	106			•	62	•	46	•
6	C_2H_5	*S*, *R*	•	114	•	106			•	64	•	43	•
7	C_2H_5	*S*, *S*	•	64			•	62	•	29	•		
8	C_2H_5	*S*, *R*	•	63			•	58	•	21	•		
1	CH_3	*S*, *S*	•	121	•	119			•	73	•		
2	CH_3	*S*, *R*	•	123	•	121			•	80	•		
3	CH_3	*S*, *S*	•	68			•	58	•	33	•		
4	CH_3	*S*, *R*	•	70			•	65	•	39	•		

The structure effect on the SmC* phase behaviour for these two pairs of compounds is interesting. The thermal stability of the SmC* phase for **5** and **6** is much higher than that of **7** and **8**. But the SmC* phase range for **5** and **6** is less sensitive than their phase transition temperature to the core molecule modification. Their SmC* temperature range is 33–44°C.

The effect of substituent on phase behaviour can be discussed in terms of the size of the substituent at the second chiral centre. The thermal stability of the mesogenic phases (except the SmC* phase of **7**) is decreased when the methyl group at the second chiral centre is substituted by an ethyl group. The effect of substituent on the temperature range of the SmC* phase is worth noting. The size of the substituent has a negligible effect on the SmC* phase range for the biphenyl ring system, 44°C for **5** vs. 46°C for **1** as well as 42°C for **6** vs. 41°C for **2**; while it widens the SmC* phase range for the naphthalene ring system, 33°C for **7** vs. 25°C for **3** as well as 37°C for **8** vs 26°C for **4**.

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