

Synthesis and Mesomorphic Properties of New Achiral Liquid Crystals with 3-Alkoxy-2-(alkoxymethyl)-1-propoxy Swallow-Tails[†]

Kyung-Tae Kang,^{*} Jeong Tak Kim, Ryeo Yun Hwang, Song Ju Park, Seng Kue Lee, Jong Gun Lee, and Yong Bae Kim[‡]

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Pusan 609-735, Korea

^{*}E-mail: kyt kang@pusan.ac.kr

[‡]Liquid Crystal Research Center and Department of Chemistry, Konkuk University, Seoul 143-710, Korea

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New liquid crystalline (biphenylcarbonyloxy)benzoates with an achiral swallow-tail derived from 3-alkoxy-2-(alkoxymethyl)-1-propanol [(ROCI₂)₂CIICI₂OII, R = Me, Et, Pr, Bu] were prepared. These liquid crystals exhibited the phase sequence (I-SmA-SmCalt-(SmCX)-Cr) and showed antiferroelectric-like Smectic C phase (SmCalt) at temperature lower, and temperature range broader than do the compounds containing a branched alkyl group as a swallow-tail. The temperature ranges of antiferroelectric phase were found to be 30-90 °C and crystallization temperatures were 4-60 °C. The binary mixture of an achiral swallow-tailed liquid crystal and a chiral antiferroelectric liquid crystal, (*S*)-MIPOBC showed antiferroelectric smectic C phase at temperature much lower than the single chiral antiferroelectric liquid crystal does.

Key Words : Liquid crystal, Swallow-tailed liquid crystal, Antiferroelectric-like phase, 3-Alkoxy-2-(alkoxy-methyl)-1-propanol

Introduction

Achiral materials with terminal swallow-tailed moieties have been demonstrated to display 'antiferroelectric-like' phase, so-called SmCalt phase, and can be used as host components of antiferroelectric mixture.¹ Chiral swallow-tailed materials derived from various types of chiral compounds were prepared and their mesomorphic properties were investigated.² However, the variation of swallow-tailed moieties has been limited to branched alkyl groups due to the synthetic problems. The investigation of chemical structure and physical property relationship is very important to liquid crystal chemistry. To meet the demand and to obtain various liquid crystalline compounds of varying physical properties a new synthetic route has to be developed.

Recently we reported the synthesis of diverse achiral swallow-tailed compounds derived from 1,3-dialkoxy-2-propanol[(ROCH₂)₂CHOH] where R is methyl, ethyl, propyl, butyl, CH₂CF₃.³ Herein we report the synthesis of new achiral swallow-tailed compounds derived from 3-alkoxy-2-(alkoxymethyl)-1-propanol and investigation of their mesomorphic properties.

Experimental Section

¹H-NMR spectra were recorded on Varian Gemini-200 (200 MHz) and Varian Inova (500 MHz) spectrometer using chloroform as an internal standard. The latter instrument was also used for recording ¹³C NMR spectra in CDCl₃ (solvent and internal reference). Elemental analyses were performed at the National Center for Inter-University Research

Facilities, Seoul National University. Phase transition temperature and phase appearance of final products were measured using polarizing microscope (Olympus BH-2) with a hot stage and a controller (Mettler FP-800-HT heating stage). Transition temperature and enthalpy were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 calorimeter. Debonylation of benzyl ethers to the corresponding alcohols and phenols were carried out in the Parr hydrogenation reactor (Parr 3916EKX).

Preparation of 2,2-dimethyl-5-(hydroxymethyl)-1,3-dioxane 3. The compounds 2 and 3 were prepared according to the literature method.⁴

Into the THF (20 mL) solution of triethyl methanetri-carboxylate (13.4 g, 57.7 mmol) was added borane-dimethyl sulfide complex in THF (5 M, 36 mL, 180 mmol) under argon atmosphere. The solution was heated under reflux for 8 h with distillation of dimethyl sulfide and THF. To the cooled solution was added methanol (60 mL) and stirred for 4 h. The solvent was removed. Addition of methanol and evaporation of volatiles were repeated (3 × 30 mL). The residue was purified by column chromatography (silica gel, chloroforms/ethanols 3:1, R_f = 0.25) to afford 2-(hydroxymethyl)propane-1,3-diol (2, 6.01 g, 98%). ¹H NMR (DMSO-d₆) δ 1.57 (sept, 1H, J = 5.9 Hz), 3.37 (dd, 6H, J = 5.9, 5.1 Hz), 4.28 (t, 3H, J = 5.1 Hz).

To a THF (130 mL) solution of 2-(hydroxymethyl)propane-1,3-diol (2, 4.05 g, 38.2 mmol) containing 4-toluene-sulfonic acid monohydrate (0.28 g, 1.45 mmol) was added 2,2-dimethoxypropane (6.6 mL, 5.59 g, 53.7 mmol). The solution was stirred for 3 h at room temperature and was neutralized by adding of triethylamine (2.6 mL, 1.89 g, 18.6 mmol). The solvent was removed and the residue was chromatographed on silica gel (chloroform/ethanol 10:1, R_f = 0.54) to give 3 (5.17 g, 93%). ¹H NMR δ 1.40 (s, 3H), 1.45

[†]This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

(s, 3H), 1.81-1.87 (m, 2H), 3.70-3.82 (m, 4H), 4.03 (dd, 2H, $J = 12.1, 4.0$ Hz).

Preparation of 2,2-dimethyl-5-(benzyloxymethyl)-1,3-dioxane 4. Sodium hydride (60% in mineral oil, 0.42 g, 10.6 mmol) was added to a dry, two-necked round-bottomed flask equipped with a rubber septum, and was washed with THF (2×10 mL). THF was removed to give NaH as a white powder. The alcohol **3** (1.03 g, 7.05 mmol) in DMF was added to the flask. After an hour of stirring at room temperature, benzyl bromide (2.40 g, 14.1 mmol) was added. The reaction mixture was refluxed for 12 h. The reaction was quenched with water and the solution was extracted with diethyl ether. The combined organic layer was dried over Na_2SO_4 , filtered, and concentrated. The residue was chromatographed on silica gel (hexanes/ether 1:1, $R_f = 0.50$) to afford **4** (1.42 g, 86.0%). $^1\text{H NMR } \delta$ 1.37 (s, 3H), 1.41 (s, 3H), 2.16-2.29 (m, 1H), 3.72 (dd, 2H, $J = 11.9, 4.6$ Hz), 3.99 (dd, 2H, $J = 11.9, 4.6$ Hz), 4.25 (d, 2H, $J = 7.3$ Hz), 5.14 (s, 2H), 7.29-7.38 (m, 5H).

Preparation of 2-(benzyloxymethyl-propane)-1,3-diol 5. To an ethanol (3 mL) solution of the benzyl ether **4** (2.36 g, 10.0 mmol) was added 5 mL of 3 N aqueous HCl and the mixture stirred at room temperature for 1 hr. The solvent ethanol was evaporated and the residue was extracted with ether. Purification by column chromatography (silica gel, chloroform/ethanol 10:1, $R_f = 0.55$) gave 2-(benzyloxymethyl)-propane-1,3-diol (**5**, 1.94 g, 99.0%). $^1\text{H NMR } \delta$ 2.03 (sept, 1H, $J = 5.5$ Hz), 2.82 (br s, 2H), 3.60 (d, 2H, $J = 5.5$ Hz), 3.80 (d, 4H, $J = 5.5$ Hz), 4.50 (s, 2H), 7.25-7.35 (m, 5H).

Preparation of 1,3-dialkoxy-2-(benzyloxymethyl)propanes 6. The synthesis of **6a** is typical. To a suspension of sodium hydride (60% in mineral oil, 0.39 g, 9.75 mmol) in THF (5 mL) was added a THF (3 mL) solution of the diol **5** (0.64 g, 3.25 mmol) and the mixture stirred for 1 h at room temperature. Methyl iodide (0.28 g, 19.5 mmol) was added to the resulting solution and the mixture was refluxed for 24 h. The reaction was quenched with water and the crude product was extracted with ether. The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated. The residue was chromatographed on silica gel (hexanes/ether 1:1, $R_f = 0.62$) to afford **6a** (0.61 g, 84.3%). Compound **6b-6d** were prepared similarly.

6a: $^1\text{H NMR } \delta$ 2.16-2.29 (m, 1H), 3.34 (s, 6H), 3.47 (d, 4H, $J = 6.2$ Hz), 3.54 (d, 2H, $J = 5.9$ Hz), 4.53 (s, 2H), 7.29-7.38 (m, 5H). **6b:** $^1\text{H NMR } \delta$ 1.17 (t, 6H, $J = 7.1$ Hz) 2.04-2.22 (m, 1H), 3.40-3.55 (m, 10H), 4.49 (s, 2H), 7.27-7.34 (m, 5H). **6c:** $^1\text{H NMR } \delta$ 0.91 (t, 6H, $J = 7.1$ Hz), 1.48-1.67 (m, 4H), 2.19-2.28 (m, 1H), 3.37 (t, 4H, $J = 6.6$ Hz), 3.40-3.59 (m, 6H), 4.52 (s, 2H), 7.27-7.41 (m, 5H). **6d:** $^1\text{H NMR } \delta$ 0.92 (t, 6H, $J = 7.3$ Hz), 1.23-1.35 (m, 4H), 1.38-1.54 (m, 4H), 2.18-2.24 (sept, 1H, $J = 5.9$ Hz), 3.41 (t, 4H, $J = 6.2$ Hz), 3.48 (d, 4H, $J = 5.9$ Hz), 3.54 (d, 2H, $J = 5.9$ Hz), 4.51 (s, 2H), 7.26-7.38 (m, 5H).

Preparation of 3-alkoxy-2-(alkoxymethyl)-1-propanols 7. The synthesis of **7a** is typical. To a methanol (5 mL) solution of **6a** (0.60 g, 2.68 mmol), 5% Pd-C catalyst (0.10

g) was added. The mixture was shaken at room temperature for 3 h under hydrogen atmosphere. The resulting mixture was filtered and washed with ether. The filtrate and washings were combined and concentrated. Chromatography on silica gel (hexanes/ether 1:1, $R_f = 0.32$) gave 3-methoxy-2-(methoxymethyl)-1-propanol (**7a**, 0.30 g, 82.6%). Compound **7b-7d** were prepared similarly.

7a: $^1\text{H NMR } \delta$ 2.06-2.16 (m, 1H) 2.61 (br s, 1H), 3.33 (s, 6H), 3.47 (d, 4H, $J = 6.2$ Hz), 3.74 (d, 2H, $J = 4.8$ Hz). **7b:** $^1\text{H NMR } \delta$ 1.18 (t, 6H, $J = 7.1$ Hz) 2.03-2.16 (m, 1H) 2.54 (br s, 1H), 3.42-3.55 (m, 8H), 3.76 (d, 2H, $J = 4.76$). **7c:** $^1\text{H NMR } \delta$ 0.89 (t, 6H, $J = 7.3$ Hz), 1.57 (m, 4H), 2.06-2.12 (m, 1H), 2.56 (br s, 1H), 3.37 (t, 4H, $J = 6.6$ Hz), 3.52 (m, 4H), 3.75 (d, 2H, $J = 4.8$ Hz). **7d:** $^1\text{H NMR } \delta$ 0.93 (t, 6H, $J = 7.0$ Hz), 1.28-1.39 (m, 4H), 1.40-1.63 (m, 4H), 2.06-2.17 (m, 1H), 2.52 (br s, 1H), 3.44 (t, 4H, $J = 6.2$ Hz), 3.54 (m, 4H), 3.78 (d, 2H, $J = 5.1$ Hz).

Preparation of 3-alkoxy-2-(alkoxymethyl)-1-propyl 4-benzyloxybenzoates 9. The synthesis of **9a** is typical. To a dichloromethane (4 mL) solution of N,N -dicyclohexylcarbodiimide (DCC, 0.32 g, 1.55 mmol) and 4-dimethylaminopyridine (DMAP, 0.10 g, 0.82 mmol) were added 4-benzyloxybenzoic acid (**8**, 0.33 g, 1.44 mmol) and the alcohol **7a** (0.18 g, 1.31 mmol). The reaction mixture was heated to reflux for 1 day. The precipitates were filtered and washed with dichloromethane. The filtrate was washed with aqueous NaHCO_3 solution and then dried (Na_2SO_4), concentrated. The residue was purified by column chromatography (silica gel, hexane/ether 1:1, $R_f = 0.60$) to afford **9a** (0.33 g, 71.2%). Compound **9b-9d** were prepared similarly.

9a: $^1\text{H NMR } \delta$ 2.35 (sept, 1H, $J = 6.2$ Hz), 3.37 (s, 6H), 3.51 (d, 4H, $J = 6.2$ Hz), 4.37 (d, 2H, $J = 6.2$ Hz), 5.14 (s, 2H), 7.02 (d, 2H, $J = 8.8$ Hz), 7.38-7.46 (m, 4H), 8.01 (d, 2H, $J = 8.8$ Hz). **9b:** $^1\text{H NMR } \delta$ 1.20 (t, 6H, $J = 7.0$ Hz), 2.37 (sept, 1H, $J = 5.9$ Hz), 3.42-3.54 (m, 8H), 4.39 (d, 2H, $J = 5.9$ Hz), 5.14 (s, 2H), 7.02 (d, 2H, $J = 8.8$ Hz), 7.38-7.46 (m, 5H), 8.01 (d, 2H, $J = 8.8$ Hz). **9c:** $^1\text{H NMR } \delta$ 0.92 (t, 6H, $J = 7.5$ Hz), 1.50-1.66 (m, 4H), 2.36 (sept, 1H, $J = 5.9$ Hz), 3.39 (t, 4H, $J = 6.6$ Hz), 3.55 (d, 4H, $J = 5.9$ Hz), 4.39 (d, 2H, $J = 5.9$ Hz), 5.14 (s, 2H), 7.01 (d, 2H, $J = 8.8$ Hz), 7.38-7.47 (m, 5H), 8.00 (d, 2H, $J = 8.8$ Hz). **9d:** $^1\text{H NMR } \delta$ 0.94 (t, 6H, $J = 7.3$ Hz), 1.30-1.46 (m, 4H), 1.51-1.65 (m, 4H), 2.39.4 (sept, 1H, $J = 5.9$ Hz), 3.45 (t, 4H, $J = 6.4$ Hz), 3.56 (d, 4H, $J = 5.9$ Hz), 4.40 (d, 2H, $J = 5.9$ Hz), 5.14 (s, 2H), 7.02 (d, 2H, $J = 9.2$ Hz), 7.35-7.48 (m, 5H), 8.03 (d, 2H, $J = 9.2$ Hz).

Preparation of 3-alkoxy-2-(alkoxymethyl)-1-propyl 4-hydroxybenzoates 10. The synthesis of **10a** is typical. To a solution of **9a** (0.32 g, 0.93 mmol) in methanol (5 mL) 5% Pd-C catalyst (0.10 g) was added. The mixture was shaken at room temperature for 3 h under hydrogen. The mixture was filtered and washed with ether. The filtrate and washings were concentrated and chromatographed on silica gel (hexanes/ether 1:1, $R_f = 0.32$) to give 3-methoxy-2-(methoxymethyl)-1-propyl 4-hydroxybenzoate (**10a**, 0.21 g, 89.0%). Compound **10b-10d** were prepared similarly.

10a: $^1\text{H NMR } \delta$ 2.31-2.41 (m, 1H), 3.35 (s, 6H), 3.51 (d, 4H, $J = 5.9$ Hz), 4.35 (d, 2H, $J = 6.2$ Hz), 6.84 (d, 2H, $J = 8.8$

Hz), 7.91 (d, 2H, $J = 8.8$ Hz). **10b**: $^1\text{H NMR}$ δ 1.20 (t, 6H, $J = 7.0$ Hz), 2.34-2.42 (m, 1H), 3.47-3.59 (m, 8H), 4.39 (d, 2H, $J = 5.9$ Hz), 6.85 (d, 2H, $J = 8.8$ Hz), 7.91 (d, 2H, $J = 8.8$ Hz). **10c**: $^1\text{H NMR}$ δ 0.92 (t, 6H, $J = 7.5$ Hz), 1.51-1.68 (m, 4H), 2.39 (sept, 1H, $J = 5.9$ Hz), 3.41 (t, 4H, $J = 6.6$ Hz), 3.57 (d, 4H, $J = 5.9$ Hz), 4.38 (d, 2H, $J = 5.9$ Hz), 6.86 (d, 2H, $J = 8.8$ Hz), 7.92 (d, 2H, $J = 8.8$ Hz). **10d**: $^1\text{H NMR}$ δ 0.94 (t, 6H, $J = 7.3$), 1.30-1.46 (m, 4H), 1.51-1.65 (m, 4H), 2.39 (sept, 1H, $J = 5.9$ Hz), 3.45 (t, 4H, $J = 6.4$ Hz), 3.56 (d, 4H, $J = 5.9$ Hz), 4.40 (d, 2H, $J = 5.9$ Hz), 6.86 (d, 2H, $J = 9.2$ Hz), 7.91 (d, 2H, $J = 9.2$ Hz).

Preparation of 3-alkoxy-2-(alkoxymethyl)-1-propyl 4-(4'-alkoxybiphenyl-4-carboxyloxy)benzoates 12. The synthesis of **12a** is typical. To a solution of 4-hydroxybenzoate **10a** (0.20 g, 0.79 mmol), DCC (0.20 g, 0.97 mmol), and DMAP (0.08 g, 0.65 mmol) was added 4-(4'-octyloxyphenyl)benzoic acid (**11a**, 0.29 g, 0.88 mmol). The reaction mixture was refluxed for 1 day. The precipitate was filtered and washed with dichloromethane. The filtrate was washed with aqueous NaHCO_3 solution, dried (Na_2SO_4), and concentrated. The crude product was chromatographed on silica gel (hexanes/ether 1:1, $R_f = 0.53$) to give **12a** (0.35 g, 78.5%). Compound **12b-12h** were prepared similarly.

12a (8CCMe): $^1\text{H NMR}$ δ 0.91 (t, 3H, $J = 7.0$ Hz), 1.31-1.59 (m, 10H), 1.75-1.84 (m, 2H), 2.40 (sept, 1H, $J = 5.9$ Hz), 3.38 (s, 6H), 3.53 (d, 4H, $J = 5.9$ Hz), 4.04 (t, 2H, $J = 6.6$ Hz), 4.43 (d, 2H, $J = 5.9$ Hz), 7.03 (d, 2H, $J = 8.8$ Hz), 7.34 (d, 2H, $J = 8.8$ Hz), 7.62 (d, 2H, $J = 8.8$ Hz), 7.72 (d, 2H, $J = 8.4$ Hz), 8.15 (d, 2H, $J = 8.8$ Hz), 8.25 (d, 2H, $J = 8.8$ Hz); $^{13}\text{C-NMR}$ δ 165.4, 164.3, 159.3, 154.4, 146.0, 131.6, 131.0, 130.6, 128.2, 127.7, 126.8, 126.5, 121.7, 114.8, 70.8, 68.2, 63.5, 59.1, 39.6, 32.0, 29.5, 29.4, 26.2, 22.9, 14.3; Anal. calc. for $\text{C}_{34}\text{H}_{42}\text{O}_7$: C 72.57, H 7.52; found: C 72.51, H 7.53.

12b (9CCMe): $^1\text{H NMR}$ δ 0.88 (t, 3H, $J = 6.6$ Hz), 1.27-1.57 (m, 12H), 1.78-1.81 (m, 2H), 2.35-2.41 (m, 1H), 3.35 (s, 6H), 3.51 (d, 4H, $J = 6.2$ Hz), 4.01 (t, 2H, $J = 6.6$ Hz), 4.40 (d, 2H, $J = 5.9$ Hz), 7.00 (d, 2H, $J = 8.8$ Hz), 7.32 (d, 2H, $J = 8.8$ Hz), 7.60 (d, 2H, $J = 8.8$ Hz), 7.70 (d, 2H, $J = 8.8$ Hz), 8.12 (d, 2H, $J = 8.8$ Hz), 8.23 (d, 2H, $J = 8.8$ Hz); $^{13}\text{C-NMR}$ δ 165.7, 164.6, 159.7, 154.8, 146.3, 131.9, 131.2, 130.8, 128.4, 128.0, 127.1, 126.7, 121.8, 115.1, 70.9, 68.2, 63.6, 59.1, 39.6, 31.9, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1; Anal. calc. for $\text{C}_{35}\text{H}_{44}\text{O}_7$: C 72.89, H 7.69; found: C 72.99, H 7.77.

12c (10CCMe): $^1\text{H NMR}$ δ 0.90 (t, 3H, $J = 6.4$ Hz), 1.30-1.62 (m, 14H), 1.76-1.87 (m, 2H), 2.37-2.46 (m, 1H), 3.38 (s, 6H), 3.53 (d, 4H, $J = 6.2$ Hz), 4.04 (t, 2H, $J = 6.6$ Hz), 4.42 (d, 2H, $J = 5.9$ Hz), 7.02 (d, 2H, $J = 8.8$ Hz), 7.34 (d, 2H, $J = 8.8$ Hz), 7.62 (d, 2H, $J = 8.8$ Hz), 7.72 (d, 2H, $J = 8.4$ Hz), 8.14 (d, 2H, $J = 8.8$ Hz), 8.25 (d, 2H, $J = 8.4$ Hz); $^{13}\text{C-NMR}$ δ 165.4, 164.3, 159.3, 154.4, 146.0, 131.6, 131.0, 130.6, 128.2, 127.7, 126.7, 126.5, 121.7, 114.8, 70.8, 68.2, 63.5, 59.1, 39.6, 32.1, 29.7, 29.6, 29.5, 29.4, 26.2, 22.9, 14.4; Anal. calc. for $\text{C}_{36}\text{H}_{46}\text{O}_7$: C 73.19, H 7.85; found: C 73.47, H 7.95.

12d (9CCEt): $^1\text{H NMR}$ δ 0.89 (t, 3H, $J = 7.0$ Hz), 1.19 (t, 6H, $J = 7.0$ Hz), 1.12-1.51 (m, 12H), 1.78-1.85 (m, 2H),

2.35-2.41 (m, 1H), 3.44-3.56 (m, 8H), 4.01 (t, 2H, $J = 6.6$ Hz), 4.42 (d, 2H, $J = 5.9$ Hz), 7.00 (d, 2H, $J = 8.8$ Hz), 7.32 (d, 2H, $J = 8.8$ Hz), 7.60 (d, 2H, $J = 8.8$ Hz), 7.70 (d, 2H, $J = 8.8$ Hz), 8.12 (d, 2H, $J = 8.8$ Hz), 8.23 (d, 2H, $J = 8.4$ Hz); $^{13}\text{C-NMR}$ δ 165.8, 159.7, 154.7, 146.3, 131.9, 131.2, 130.8, 129.1, 128.4, 128.0, 127.1, 126.7, 121.8, 115.1, 68.7, 68.2, 66.6, 63.9, 39.7, 31.9, 29.6, 29.4, 29.3, 26.1, 22.7, 15.1, 14.1; Anal. calc. for $\text{C}_{37}\text{H}_{48}\text{O}_7$: C 73.48, H 8.00; found: C 73.23, H 8.06.

12e (10CCEt): $^1\text{H NMR}$ δ 0.90 (t, 3H, $J = 5.9$ Hz), 1.21 (t, 6H, $J = 6.4$ Hz), 1.29-1.76 (m, 14H), 1.84-1.89 (m, 2H), 2.37-2.46 (m, 1H), 3.46-3.72 (m, 8H), 4.03 (t, 2H, $J = 6.6$ Hz), 4.44 (d, 2H, $J = 5.9$ Hz), 7.03 (d, 2H, $J = 8.8$ Hz), 7.34 (d, 2H, $J = 8.8$ Hz), 7.62 (d, 2H, $J = 8.4$ Hz), 7.72 (d, 2H, $J = 8.1$ Hz), 8.15 (d, 2H, $J = 8.4$ Hz), 8.25 (d, 2H, $J = 8.4$ Hz); $^{13}\text{C-NMR}$ δ 165.8, 164.6, 159.7, 154.7, 146.3, 131.9, 131.2, 130.8, 128.4, 128.1, 127.1, 126.7, 121.8, 115.1, 68.7, 68.2, 66.6, 63.9, 39.7, 31.9, 29.5, 29.4, 29.3, 29.2, 26.1, 22.7, 15.1, 14.1; Anal. calc. for $\text{C}_{38}\text{H}_{50}\text{O}_7$: C 73.76, H 8.14; found: C 74.15, H 8.28.

12f (9CCPr): $^1\text{H NMR}$ δ 0.87-0.95 (m, 9H), 1.28-1.66 (m, 16H), 1.81-1.84 (m, 2H), 2.36-2.41 (m, 1H), 3.39 (t, 4H, $J = 6.6$ Hz), 3.54 (d, 4H, $J = 6.6$ Hz), 4.01 (t, 2H, $J = 6.6$ Hz), 4.42 (d, 2H, $J = 5.9$ Hz), 7.00 (d, 2H, $J = 8.8$ Hz), 7.32 (d, 2H, $J = 8.8$ Hz), 7.65 (d, 2H, $J = 8.8$ Hz), 7.70 (d, 2H, $J = 8.8$ Hz), 8.15 (d, 2H, $J = 8.8$ Hz), 8.23 (d, 2H, $J = 8.8$ Hz); $^{13}\text{C-NMR}$ δ 165.4, 164.3, 159.3, 154.4, 146.0, 131.6, 131.0, 130.6, 128.2, 127.8, 126.8, 126.5, 121.6, 114.8, 73.0, 68.8, 68.2, 63.9, 39.8, 32.0, 29.7, 29.6, 29.4, 26.2, 23.0, 22.9, 14.3, 10.8; Anal. calc. for $\text{C}_{39}\text{H}_{52}\text{O}_7$: C 74.02, H 8.28; found: C 73.75, H 8.42.

12g (10CCPr): $^1\text{H NMR}$ δ 0.87-0.97 (m, 9H), 1.29-1.69 (m, 18H), 1.80-1.87 (m, 2H), 2.38-2.44 (m, 1H), 3.41 (t, 4H, $J = 6.6$ Hz), 3.56 (d, 4H, $J = 6.2$ Hz), 4.03 (t, 2H, $J = 6.4$ Hz), 4.44 (d, 2H, $J = 5.9$ Hz), 7.02 (d, 2H, $J = 8.8$ Hz), 7.34 (d, 2H, $J = 8.8$ Hz), 7.62 (d, 2H, $J = 8.4$ Hz), 7.72 (d, 2H, $J = 8.4$ Hz), 8.15 (d, 2H, $J = 8.4$ Hz), 8.25 (d, 2H, $J = 8.4$ Hz); $^{13}\text{C-NMR}$ δ 165.4, 164.3, 159.3, 154.3, 146.0, 131.6, 130.9, 130.6, 128.2, 127.8, 126.7, 126.4, 121.6, 114.8, 73.0, 68.8, 68.2, 63.8, 39.7, 32.0, 29.7, 29.54, 29.47, 29.4, 26.2, 23.0, 22.9, 14.3, 10.8; Anal. calc. for $\text{C}_{40}\text{H}_{54}\text{O}_7$: C 74.27, H 8.41; found: C 74.29, H 8.54.

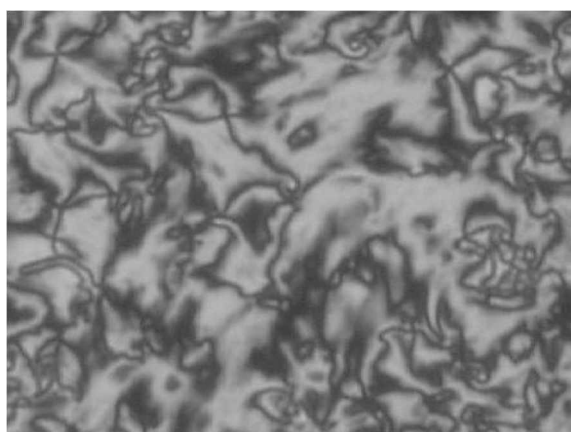
12h (10CCBu): $^1\text{H NMR}$ δ 0.87-0.96 (m, 9H), 1.30-1.63 (m, 22H), 1.80-1.87 (m, 2H), 2.37-2.43 (m, 1H), 3.45 (t, 4H, $J = 6.6$ Hz), 3.56 (d, 4H, $J = 6.6$ Hz), 4.04 (t, 2H, $J = 6.6$ Hz), 4.44 (d, 2H, $J = 5.9$ Hz), 7.03 (d, 2H, $J = 8.8$ Hz), 7.34 (d, 2H, $J = 8.8$ Hz), 7.62 (d, 2H, $J = 8.8$ Hz), 7.72 (d, 2H, $J = 8.8$ Hz), 8.15 (d, 2H, $J = 8.8$ Hz), 8.25 (d, 2H, $J = 8.8$ Hz); $^{13}\text{C-NMR}$ δ 165.4, 164.3, 159.3, 154.3, 146.0, 131.6, 130.9, 130.6, 128.2, 127.8, 126.8, 126.4, 121.6, 114.8, 71.1, 68.8, 68.2, 63.8, 39.7, 32.0, 31.9, 29.7, 29.55, 29.47, 29.4, 26.2, 1, 22.9, 19.5, 14.3, 14.1; Anal. calc. for $\text{C}_{42}\text{H}_{58}\text{O}_7$: C 74.74, H 8.66; found: C 74.36, H 8.74.

Results and Discussion

Synthesis of new achiral swallow-tailed liquid crystals

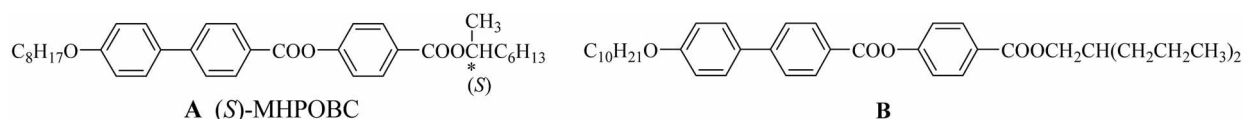
Table 1. Phase transition temperatures (°C) and enthalpies ($\Delta H/kJmol^{-1}$)(*in italics*) for the 3-alkoxy-2-(alkoxymethyl)-1-propyl 4-(4'-alkoxybiphenyl-4-carboxyloxy)benzoates **12** on cooling

Compound	mp	Cr	SmCX	SmCalt	SmC	SmA	I
12a (8CCMe)	85.3	•	36.9	•	56.8	•	148.3
			<i>7.35</i>		<i>0.26</i>		<i>4.01</i>
12b (9CCMe)	86.2	•	59.1	–	115.0	•	141.4
			<i>17.4</i>		<i>0.10</i>		<i>3.57</i>
12c (10CCMe)	79.1	•	38.0	–	113.8	•	138.3
			<i>12.4</i>		<i>0.23</i>		<i>4.10</i>
12d (9CCEt)	72.9	•	45.1	–	104.7	•	127.8
			<i>3.29</i>		<i>0.07</i>		<i>3.81</i>
12e (10CCEt)	56.2	•	11.4	–	–	•	121.3
			<i>7.41</i>			<i>0.10</i>	<i>5.03</i>
12f (9CCPr)	71.3	•	46.6	•	58.8	•	117.0
			<i>18.2</i>		<i>0.04</i>		<i>0.13</i>
12g (10CCPr)	46.1	•	3.8	•	58.7	•	111.5
			<i>12.0</i>		<i>0.05</i>		<i>0.29</i>
12h (10CCBu)	45.6	•	8.6	–	89.6	•	109.0
			<i>13.7</i>		<i>0.22</i>		<i>3.10</i>

**Figure 1.** Schlieren texture of the SmCalt phase observed in **12g** (10CCPr) at 75.0 °C on cooling exhibits both two- and four-brush singularities.

into a clean glass vial, and dissolved with anhydrous dichloromethane. The dichloromethane was then evaporated and the last trace of solvent was under vacuum.

The DSC data for the bisalkoxy swallow-tailed compound **12g** (10CCPr), the branched alkyl chain swallow-tailed material (**B**), and the binary mixtures of each of them with the chiral antiferroelectric liquid crystal [(*S*)-MHPOBC, **A**] were summarized in Table 2. The binary mixture of the chiral (*S*)-MHPOBC (**A**) with the bisalkoxy swallow-tailed liquid crystal (**12g**) showed a phase sequence of I-SmA-SmC_A-SmCX-Cr. Its temperature range of SmC_A was much broader than that of the binary mixture of the compound containing a branched alkyl swallow-tail (**B**) and the chiral liquid crystal **A**.^{1d} In this particular case the smectic A phase exhibited a focal conic texture and the SmC_A* phase were characterized by the schlieren texture with two- and four brush singularities shown in Figure 2.

Table 2. The transition temperatures and associated enthalpies ($\Delta H/kJmol^{-1}$)(*in italics*) for the binary mixtures of **A** with **12g** (10CCPr) and **A** with **B**

Code	Cr	SmCx	SmCalt/SmC _A *	SmC/SmC*	SmA	I
12g (10CCPr)	•	3.8	•	58.7	•	111.5
		<i>12.0</i>		<i>0.05</i>		<i>0.29</i>
B	•	60.4	–	116.2	•	136.9
		<i>68.3</i>		<i>1.4</i>		<i>9.9</i>
12g 85%/A15%	•	–1.8	•	26.5	•	122.5
		<i>3.2</i>		<i>0.06</i>		<i>0.11</i>
B 85%/A15%	•	49.9	–	119.2	•	140.3
		<i>52.4</i>		<i>1.8</i>		<i>12.5</i>
A	•	73.5	–	121.0	•	151.5

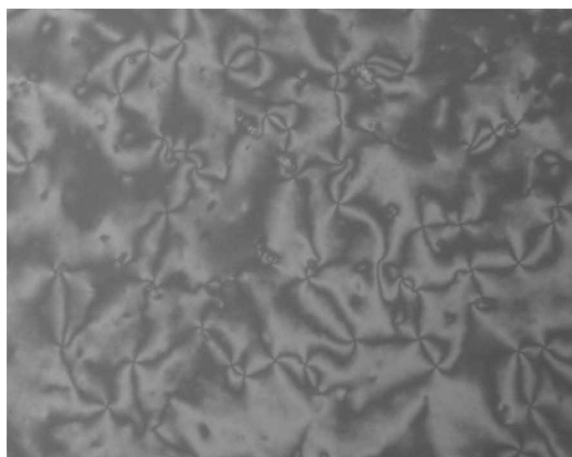


Figure 2. The schlieren texture of the Sm_{CA}^* phase observed in the mixture **12g85/A15** shows two- and four-brush singularities.

Conclusion

New achiral swallow-tailed liquid crystals derived from 3-alkoxy-2-(alkoxymethyl)-1-propanol were prepared in good yields. These liquid crystals exhibit antiferroelectric-like smectic C phase at temperature lower than and temperature range broader than does compound bearing the corresponding branched alkyl swallow-tails. Investigation of the binary mixtures with a chiral antiferroelectric liquid crystal

indicates that new achiral liquid crystals with bisalkoxy swallow-tails can be more useful as host components of antiferroelectric mixture.

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