

## Synthesis and Mesomorphic Properties of Achiral Liquid Crystals with 1,3-Dialkoxy-2-propyl Swallow-Tail

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### Abstract

Achiral swallow-tailed liquid crystals derived from 1,3-dialkoxy-2-propanol were prepared and their mesomorphic properties were investigated. 1,3-Dialkoxy-2-propyl swallow-tailed material showed antiferroelectric-like smectic C phase at lower temperature and in broader temperature range than the corresponding compounds with a branched alkyl group as a swallow-tail. They could serve as suitable host for antiferroelectric mixtures.

### 1. Introduction

Since the discovery of the antiferroelectric phase ( $S_{CA}^*$ ) in MHPOBC [4'-(1-methylheptyloxy-carbonyl)phenyl 4-octyloxybiphenyl-4-carboxylate] by Chandani *et al.*<sup>1</sup>, a large number of materials exhibiting an antiferroelectric phase have been prepared. Antiferroelectric phases were observed only in optically active derivatives of chiral secondary alcohols. However, it has been known that achiral materials with terminal swallow-tailed moieties can also have 'antiferroelectric-like' phase, a so-called  $S_{Calt}$  phase<sup>2-6</sup>. They can be doped with small quantity of antiferroelectric liquid crystal to provide antiferroelectric eutectic mixtures with lower viscosity and wider operating temperature range<sup>2-5</sup>.

Here we describe the synthesis of new achiral swallow-tailed compounds whose swallow-tailed moieties are 1,3-dialkoxy-2-propyl group instead of branched alkyl chain, and investigation of their liquid-crystalline properties.

### 2. Experimental

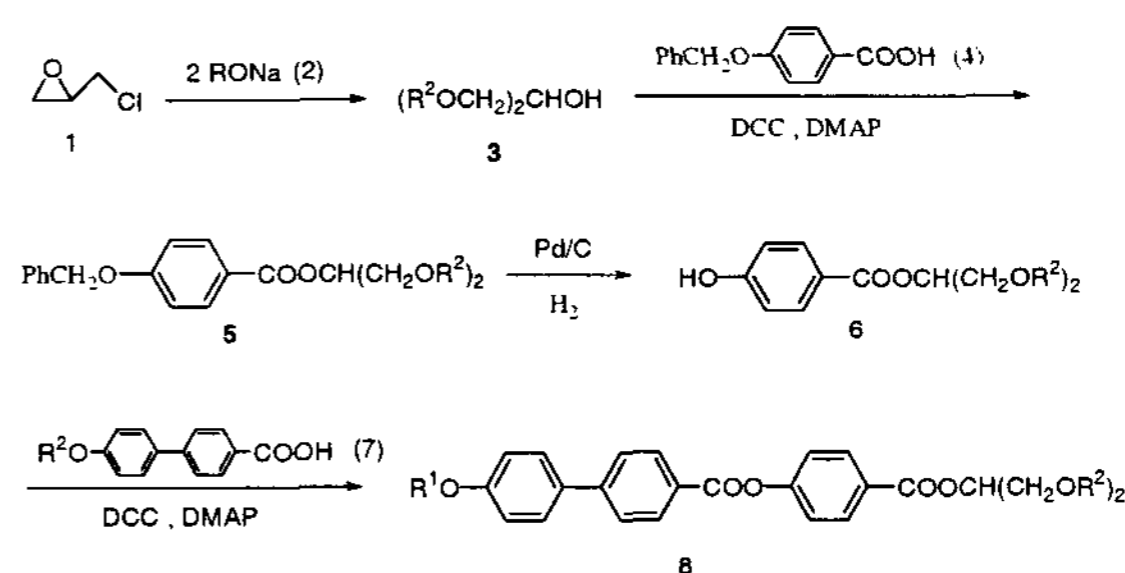
<sup>1</sup>H-NMR spectra were recorded on Varian Gemini-200 (200 MHz) and Varian Inova (500

MHz) spectrometer using chloroform as an internal standard. The latter instrument was also used for recording <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> (solvent and internal reference) and 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 by 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 Pyris Diamond DSC calorimeter.

### 3. Results and Discussion

The synthesis of new achiral swallow-tailed liquid crystals **8** derived from 1,3-dialkoxy-2-propanol (**3**) is outlined in Scheme 1.

Scheme 1



1,3-Dialkoxy-2-propanol **3** were prepared from the reaction of epichlorohydrin (**1**) with 2 equivalents of sodium alkoxide where  $R^1$  is methyl, ethyl, propyl, butyl,  $CH_2CF_3$ ,  $CH_2CF_2CF_3$  and allyl. The alcohols **3** were esterified with 4-benzyloxybenzoic acid (**4**) in the presence of

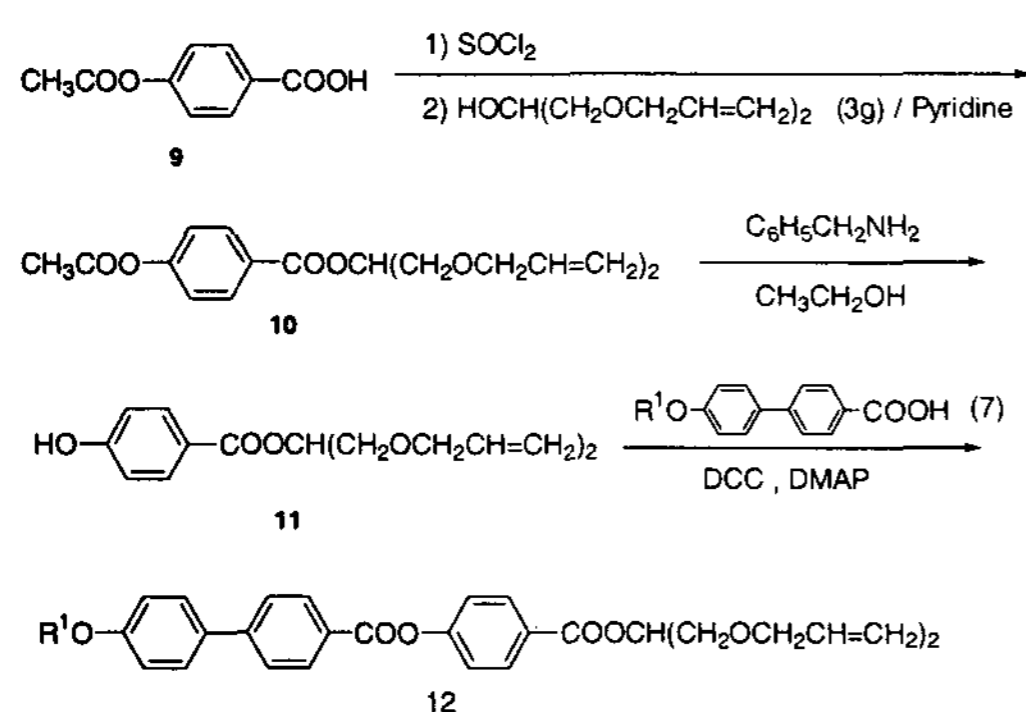
Table 1. Phase transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies ( $\text{kJ mol}^{-1}$ ) for the new achiral liquid crystals with 1,3-dialkoxy-2-propyl swallow-tail.

Abbreviation		Phase transition temperature ( $^{\circ}\text{C}$ ) and enthalpy ( $\text{kJ mol}^{-1}$ )							
		Cry.	$S_{CA}^*$	$S_C^*$	$S_A$	Iso.			
8C-Et	Heating ( $\Delta H$ )	• 84.3 (23.8)	•	96.7 (0.09)	•	99.7 (0.18)	•	122.2 (3.83)	•
	Cooling ( $\Delta H$ )	• 56.6 (19.5)	•	94.4 (0.10)	•	98.0 (0.15)	•	120.8 (4.05)	•
8C- $\text{CH}_2\text{CF}_3$	Heating ( $\Delta H$ )	• 88.9 (24.9)	•	125.4 (0.20)	-		•	138.4 (4.85)	•
	Cooling ( $\Delta H$ )	• 65.3 (20.4)	•	86.1 (0.02)	•	124.6 (0.06)	•	136.8 (4.89)	•
9C-Et	Heating ( $\Delta H$ )	• 75.0 (32.1)	•	90.0 (0.12)	•	91.6 (0.11)	•	110.9 (3.22)	•
	Cooling ( $\Delta H$ )	• 48.0 (14.5)	•	88.4 (1.14)	•	91.0 (0.13)	•	110.1 (3.25)	•
9C- $\text{CH}_2\text{CF}_3$	Heating ( $\Delta H$ )	• 84.5 (25.2)	•	86.7 (0.22)	•	113.4 (0.02)	•	123.5 (2.31)	•
	Cooling ( $\Delta H$ )	• 60.7 (22.4)	•	62.7 (0.77)	•	110.6 (0.02)	•	122.9 (3.32)	•
9C- $\text{CH}_2\text{CF}_2\text{CF}_3$	Heating ( $\Delta H$ )	• 61.2 (30.3)	•	114.6 (0.60)	-		•	128.9 (4.60)	•
	Cooling ( $\Delta H$ )	• 14.0 (11.1)	•	42.6 (0.30)	•	112.7 (0.60)	•	127.0 (4.50)	•
10C-Me	Heating ( $\Delta H$ )	• 92.4 (34.3)	-		•	106.3 (0.16)	•	124.3 (3.42)	•
	Cooling ( $\Delta H$ )	• 54.4 (26.8)	•	104.8 (0.34)	•	110.1 (0.02)	•	122.5 (4.78)	•
10C-Et	Heating ( $\Delta H$ )	• 67.2 (12.7)	•	83.2 (0.02)	•	104.4 (0.33)	•	113.5 (4.51)	•
	Cooling ( $\Delta H$ )	• 43.3 (36.1)	•	76.8 (0.02)	•	97.4 (0.40)	•	111.9 (2.72)	•
10C-Pr	Heating ( $\Delta H$ )	• 60.9 (30.3)	•	80.3 (0.25)	-		•	99.6 (2.53)	•
	Cooling ( $\Delta H$ )	• 31.3 (19.8)	•	80.2 (0.26)	-		•	97.5 (2.64)	•
10C-Bu	Heating ( $\Delta H$ )	• 55.6 (26.9)	•	76.6 (3.45)	-		•	99.9 (2.62)	•
	Cooling ( $\Delta H$ )	• 27.8 (25.5)	•	63.1 (0.02)	•	75.5 (0.21)	•	97.2 (3.32)	•
10C-Allyl	Heating ( $\Delta H$ )	• 55.2 (41.8)	•	83.4 (0.20)	-		•	109.2 (5.50)	•
	Cooling ( $\Delta H$ )	• 10.7 (22.1)	•	79.8 (0.40)	-		•	107.8 (5.90)	•
10C- $\text{CH}_2\text{CF}_3$	Heating ( $\Delta H$ )	• 85.9 (22.8)	•	110.6 (0.07)	-		•	112.0 (2.73)	•
	Cooling ( $\Delta H$ )	• 39.7 (25.2)	•	95.3 (0.21)	•	114.1 (0.32)	•	120.1 (3.23)	•
12C-Et	Heating ( $\Delta H$ )	• 52.3 (49.5)	•	89.8 (0.24)	-		•	107.3 (3.48)	•
	Cooling ( $\Delta H$ )	• 46.9 (27.4)	•	63.3 (0.05)	•	88.7 (0.32)	•	105.8 (3.58)	•
12C- $\text{CH}_2\text{CF}_3$	Heating ( $\Delta H$ )	• 89.5 (16.2)	•	99.4 (0.05)	•	104.1 (0.53)	•	109.0 (2.89)	•
	Cooling ( $\Delta H$ )	• 64.3 (26.1)	•	95.9 (0.02)	•	102.9 (0.55)	•	107.9 (2.92)	•

1,3-dicyclohexylcarbodiimide (DCC) and N,N-dimethylaminopyridine (DMAP) to give 4-benzyloxybenzoates **5** in good yields. 4-Benzyloxybenzoates **5** were deprotected by the Pd-catalyzed hydrogenation reaction. Esterification of the resulting 4-hydroxybenzoates **6** with 4'-alkoxybiphenyl-4-carboxylic acid (**7**) in the presence of DCC and DMAP afforded the swallow-tailed liquid crystals **8** in good yield.

4-(1,3-Dialloxy-2-propyloxycarbonyl)phenyl 4'-alkoxybiphenyl-4-carboxylate was prepared via an altered route (Scheme 2). Debenzylation to regenerate phenolic OH cannot be achieved under catalytic hydrogenation conditions without saturating the olefinic double bonds within the molecule. The phenolic OH of 4-hydroxybenzoic acid was protected by acetylation with acetic anhydride and the resulting 4-acetyloxybenzoic acid **9** was esterified with 1,3-dialloxy-2-propanol (**3g**). The esterification was carried out in two steps. The acid **9** was converted to the acid chloride, which was allowed to react with 1,3-dialloxy-2-propanol to give **10**. The acetate ester **10** was deprotected with benzylamine to produce phenol **11**, which was esterified with 4-(4'-alkoxyphenyl)benzoic acid in the presence of DCC and DMAP to give the final product **12** in good yields. The structures of the products were identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, low and high mass spectrometry, and elemental analysis.

Scheme 2



Optical microscopy and differential scanning calorimetry confirmed that all the compounds prepared are enantiotropic and show antiferroelectric-like phases (Figure 1). Most compounds exhibited the phase sequence: Iso- $S_A$ - $S_C^*$ - $S_{Calt}^*$ -Cry, some of them did not show  $S_C^*$

phase. The temperature ranges of antiferroelectric phases were 20-70 °C and crystallization temperatures were 10-65 °C (Table 1).

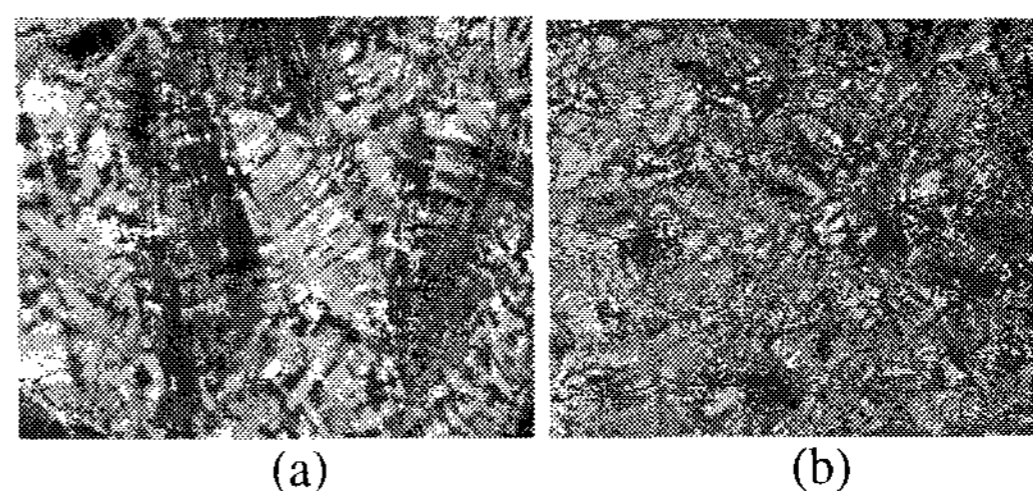


Figure 1. Optical polarizing microscopic texture observed in the striped domain texture of the antiferroelectric smectic C phase in new swallow-tailed liquid crystal. (a) **8** ( $R^1=\text{C}_{10}\text{H}_{21}$ ,  $R^2=\text{CH}_2\text{CF}_3$ ) (b) **8** ( $R^1=\text{C}_8\text{H}_{17}$ ,  $R^2=\text{CH}_2\text{CH}_3$ )

#### 4. Conclusion

New achiral swallow-tailed liquid crystals derived from 1,3-dialkoxy-2-propanol were prepared in good yields. These newly synthesized swallow-tailed liquid crystals having 1,3-dialkoxy-2-propyl moieties exhibited antiferroelectric-like smectic C phase at lower temperature and in broader temperature range than the corresponding compounds containing a branched alkyl group as a swallow-tailed moiety.

#### 5. Acknowledgements

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#### 6. References

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