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Synthesis and Thermal Properties for 4-(4-Alkoxyphenoxy-carbonyl)phenyl 3-Alkoxy-2-X-benzoates

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Some derivatives of 4-(4-alkoxyphenoxy-carbonyl)phenyl 3-alkoxy-2-X-benzoates (X=F, Cl, Br, or CF₃) were synthesized by means of an ortho-directed lithiation followed by an electrophilic aromatic substitution reaction, as a key step, and their thermal properties of liquid crystals were examined. These results are discussed in terms of molecular structure and electrostatic effects.

Keywords: binary phase diagram; lateral substituent; liquid crystals; nematic phase; synthesis

INTRODUCTION

It has been well known that the linearity of the molecular shape is one of important factors in exhibiting liquid crystal (LC) properties. Therefore, the introduction of the lateral substituent to the LC molecule is avoided in practical LC materials, though it sometimes modifies the phase sequence as well as dielectric anisotropy [1–3].

Recently, we revealed that the LC molecules with the lateral alkoxy substituent exhibit a smectic A (SmA) and/or smectic C (SmC) properties, and mentioned the conformational effect of the lateral alkoxy group on mesomorphic properties [4–7]. However, the influence of

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the lateral substituent on mesomorphic properties is not yet clear. Accordingly, compounds **1–5** were synthesized to study the effect of the lateral substituents on mesomorphic properties, shown below.

EXPERIMENTALS

Method

The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp = 156.6°C, 28.4 J/g). The DSC thermogram was operated at a heating or cooling rate of 5°C min⁻¹. The mesophases were characterized by a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). ¹H NMR spectra were measured using a JEOL EX-270 spectrometer, where TMS was used as an internal standard. IR spectra were recorded with a Horiba FT-200 infrared spectrometer. The purity was checked by HPLC.

MATERIALS

Compounds **1–5** (Figure 1) were synthesized in a moderate yield according to Schemes 1–3, where an *ortho*-directed lithiation and subsequent electrophilic aromatic substitution reaction, as a key step.

For the synthesis of compounds **1** and **5**, treatment of 2-*X-n*-hexyloxybenzene (X = F or CF₃) with a equivalent of *n*-butyllithium afforded an aryllithium species, which was quenched with carbon dioxide to give the corresponding carboxylic acid on acidification in a moderate yield (Scheme 1). In these reactions, the fluoro substituent is indispensable for the directing group of the *ortho*-lithiations.

For compounds **2–4**, treatment of 3-methoxymethoxybenzyl alcohol, prepared by methoxymethylation of ethyl 3-hydroxybenzoate and the

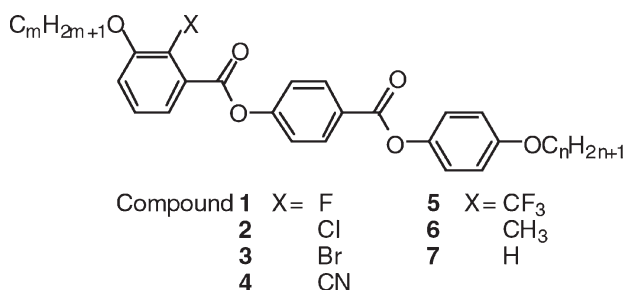
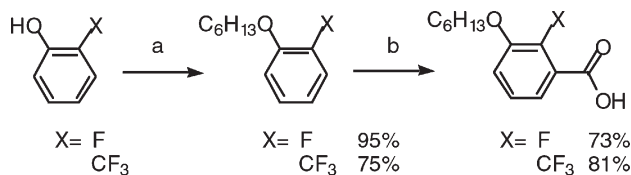


FIGURE 1 Chemical structures for compounds **1–7**.

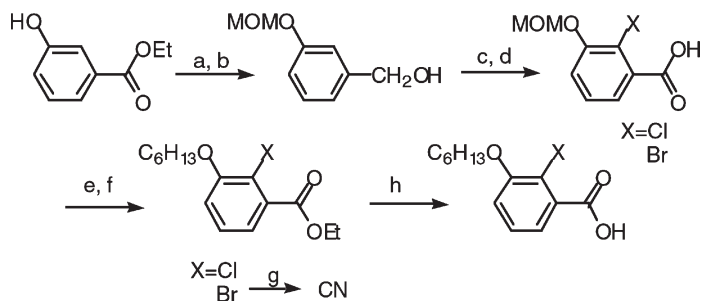


SCHEME 1 Synthesis for 3-alkoxy-2-X-benzoic acid (X = F or CF₃). Reagent and conditions: (a) C₆H₁₃Br, K₂CO₃, 3-Pentanone, reflux; (b) BuLi, THF, −78°C then CO₂.

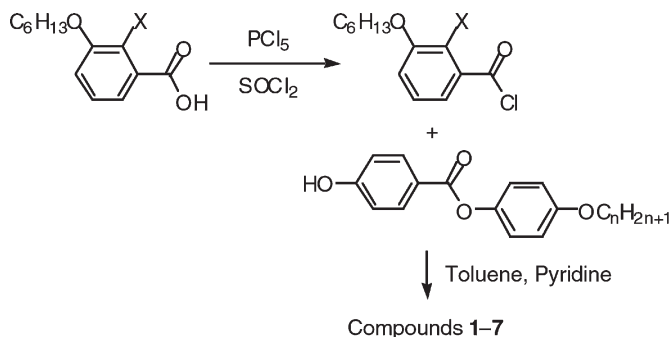
subsequent reduction of the ester, with 2 equivalents of *n*-butyllithium gave the *ortho*-lithiated aryllithium species. The species was quenched with hexachloroethane [8] for **2** or 1,2-dibromoethane [9] for **3** and **4**, to give the corresponding benzyl alcohol in a moderate yield. In all the cases shown in scheme 1 and 2, the lithiations with *n*-butyllithium followed by the electrophilic aromatic substitution reaction were carried out at low temperature (−78°C). Subsequent functional group conversions, such as oxidation, deprotection, alkylation etc, on the benzyl alcohols, gave the desired carboxylic acids, as shown in Scheme 2.

Compounds **1–5** were prepared by an esterification of the corresponding carboxylic acids and phenols. The spectra data for **1–5** are summarized in Ref. [10].

Compounds **6** and **7s** were prepared by the conventional methods described in our earlier paper [4].



SCHEME 2 Synthesis for 3-alkoxy-2-X-benzoic acid (X = Cl, Br or CN). Reagent and conditions: (a) MOMCl, NaH, THF (95%); (b) LiAlH₄, THF (90%); (c) 2BuLi, THF, −78°C then hexachloroethane (X = Cl; 70%) or 1,2-dibromoethane (X = Br; 58%); (d) KMnO₄, H₂O, acetone (X = Cl; 75%, X = Br; 66%); (e) H₂SO₄, EtOH, (X = Cl; 87%, X = Br; 62%); (f) C₆H₁₃Br, K₂CO₃ (X = Cl; 70%, X = Br; 77%); (g) CuCN, DMF (54%); (h) NaOH aq., EtOH (X = Cl; 65%, X = Br; 69%, X = CN; 45%). MOM; Methoxymethyl group.

**SCHEME 3** Synthesis for compounds 1–7.

RESULTS AND DISCUSSION

Transition temperatures and latent heats for 1–7 are summarized in Table 1.

Compounds 1, 2, and 5 show a nematic (N) phase with a schlieren and homeotropic textures under a homogeneous and homogeneous alignment glass surfaces, respectively, in a cooling process. The N–I (isotropic) transition temperatures for 1, 2, and 5 are determined to be 55, 64, and 25°C, respectively. Compounds 3 and 4, on the other hand, are non-mesogenic even in a rapid cooling process.

TABLE 1 Transition Temperatures and Latent Heats for Compounds 1–7

	Compound		Transition temperature (°C)			Latent heat (kJ/mol)	
	m	n	C	N	I	mp	N–I
1	6	6	• 63	(• 55)	•	46.3	0.4
2			• 68	(• 64)	•	34.8	*2
3a			• 67	[• 57]	•	30.5	
3b		14	• 80	–	•	48.5	
4		6	• 128	–	•	35.1	
5			• 59	(• 25)	•	33.7	0.5
6a ^{*1}			• 67	• 84	•	45.3	0.8
6b ^{*1}		14	• 79	• 81	•	58.8	1.3
7 ^{*1}	5	5	• 76	[• 22]	•	36.5	

C, N, and I indicate crystal, nematic, and isotropic phases, respectively.

Parentheses and brackets indicate a monotropic and virtual transitions, respectively.

*1, See ref. [6]; *2, The latent heat could not be detected by a DSC thermogram on rapid cooling process.

In order to determine the LC properties for **3** and **4**, the binary phase diagrams for the mixtures of **3** and 4-octyloxyphenyl 4-octyloxybenzoate (**8**), and **4** and 4-(4-hexyloxyphenoxy-carbonyl)phenyl 4-cyano-3-heptyloxybenzoates (**9**) were examined and are shown in Figure 2. The N–I transition temperature decreases gradually with increasing the concentration of **3a**, and a virtual N–I transition temperature for **3a** was estimated to be 57°C as shown in Figure 2(a). The smectic C (SmC)–N transition temperature, on the other hand, steeply decreases with increasing the concentration of **3a** and could not be observed at more than 30 mol% of **3a**. As can be seen from Figure 3(b), SmC–smectic A (SmA) and SmA–N or I transition temperatures decrease steeply with increasing the concentration of **4**, indicating mesomorphic properties for **4** are extremely low.

The effective order of the substituent (X) for the N–I phase transition temperature is expressed as follows.

T_{N-I} ; CH_3 (**6**) > Cl (**2**) > Br (**3**) > F (**1**) > CF_3 (**5**) > H (**7**), CN (**4**)

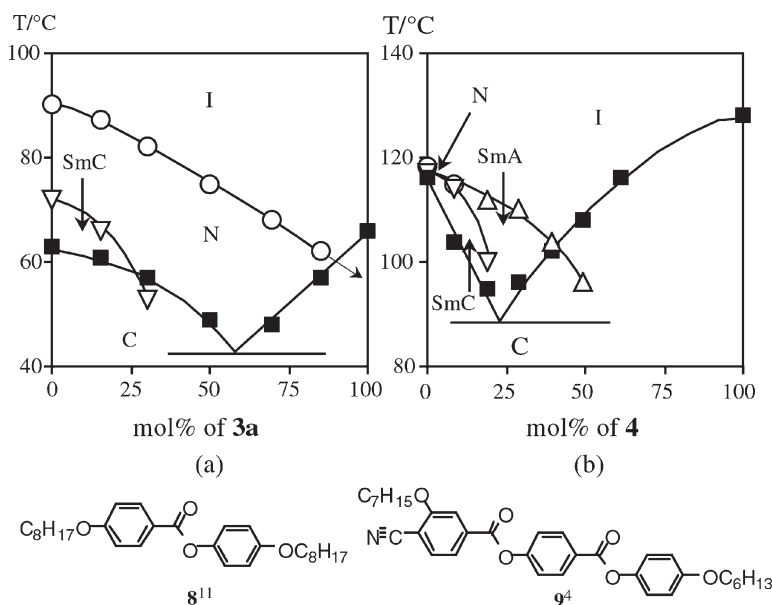


FIGURE 2 Binary phase diagrams for the mixtures; (a) 4-octyloxyphenyl 4-octyloxybenzoate (**8**) (left) and **3a** (right), and (b) 4-(4-hexyloxyphenoxy-carbonyl)phenyl 4-cyano-3-heptyloxybenzoates (**9**) (left) and **4** (right). ○; N–I, △; SmA–I, ▽; SmC–N or SmA, ■; C–SmC, N, SmA, or I. Phase transitions below a melting point are a monotropic transition.

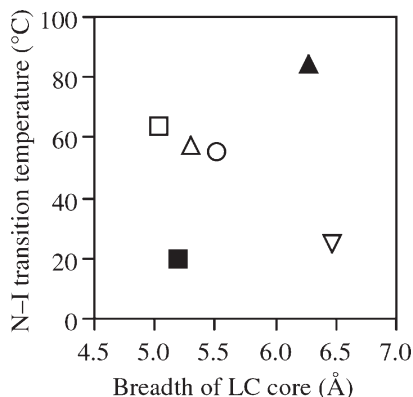


FIGURE 3 Plots of N–I transition temperature vs. breadth of LC core for 1; ○, 2; □, 3; △, 4; ▽, 6; ▲, and 7; ■.

The N–I transition temperatures and virtual ones for 1–4, 6, and 7 are plotted against the breadth of the LC cores, which are optimized by a semi-empirical molecular calculation (MOPAC) with an AM1 method [12] as shown in Figure 3.

The N–I transition temperatures for 1–4 show a good correlation with the breadth of the LC core, though those for 6 and 7 are separated from the correlation.

These results indicate that the N–I transition temperatures are influenced by not only geometrical effect, such as the breadth of the LC core, but also electrostatic one.

Further examination is now underway.

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- [10] Spectra data for 1: IR (KBr disc); $\nu=1726.0\text{ cm}^{-1}$, $^1\text{H NMR}$ (CDCl_3); $\delta=0.91$ (6H, t, $J=7.0\text{ Hz}$), 1.32–1.52 (12H, m), 1.79 (2H, quin., $J=6.5\text{ Hz}$), 1.85 (2H, qui.,

$J=6.5$ Hz), 3.96 (2H, t, $J=6.5$ Hz), 4.07 (2H, t, $J=6.5$ Hz), 6.92 (2H, d, $J=9.0$ Hz), 7.12 (2H, d, $J=9.0$ Hz), 7.18–7.20 (2H, m), 7.38 (2H, d, $J=8.5$ Hz), 7.62 (1H, m), and 8.27 (2H, d, $J=8.5$ Hz) ppm.

Spectra data for **2**: IR (KBr disc) $\nu=1735.6$ and 1741.4 cm^{-1} , ^1H NMR (CDCl_3); $\delta=0.91$ (6H, t, $J=7.0$ Hz), 1.32–1.52 (12H, m), 1.79 (2H, quin., $J=6.5$ Hz), 1.85 (2H, qui., $J=6.5$ Hz), 3.96 (2H, t, $J=6.5$ Hz), 4.07 (2H, t, $J=6.5$ Hz), 6.92 (2H, d, $J=9.0$ Hz), 7.12 (2H, d, $J=9.0$ Hz), 7.18–7.20 (2H, m), 7.38 (2H, d, $J=8.5$ Hz), 7.62 (1H, m), and 8.27 (2H, d, $J=8.5$ Hz) ppm.

Spectra data for **3a**: IR (KBr disc) $\nu=1739.5\text{ cm}^{-1}$, ^1H NMR (CDCl_3); $\delta=0.91$ (3H, t, $J=6.0$ Hz), 0.92 (3H, t, $J=6.0$ Hz), 1.32–1.59 (12H, m), 1.79 (2H, qui., $J=6.5$ Hz), 1.86 (2H, qui., $J=6.5$ Hz), 3.96 (2H, t, $J=6.5$ Hz), 4.08 (2H, t, $J=6.5$ Hz), 6.93 (2H, d, $J=8.0$ Hz), 7.07 (1H, dd, $J=8.0, 1.5$ Hz), 7.12 (2H, d, $J=8.0$ Hz), 7.37 (1H, t, $J=8.0$ Hz), 7.42 (2H, d, $J=8.0$ Hz), 7.48 (1H, dd, $J=8.0, 1.5$ Hz), and 8.27 (2H, d, $J=8.0$ Hz) ppm.

Spectra data for **4a**: IR (KBr disc) $\nu=1689.3$ and 2227 cm^{-1} , ^1H NMR (CDCl_3); $\delta=0.90$ (3H, t, $J=6.5$ Hz), 1.31–1.57 (6H, m), 1.43 (3H, t, $J=7.0$ Hz), 1.86 (2H, qui., $J=6.5$ Hz), 4.12 (2H, t, $J=6.5$ Hz), 4.44 (2H, q, $J=7.0$ Hz), 7.19 (1H, dd, $J=8.0, 1.5$ Hz), and 7.54–7.65 (2H, m) ppm.

Spectra data for **5**: IR (KBr disc); $\nu=1731.8$ and 1756.8 cm^{-1} , ^1H NMR (CDCl_3); $\delta=0.88$ (3H, t, $J=7.0$ Hz), 0.92 (3H, t, $J=7.0$ Hz), 1.24–1.54 (12H, m), 1.79 (2H, qui., $J=7.0$ Hz), 1.85 (2H, qui., $J=7.0$ Hz), 3.96 (2H, $J=6.5$ Hz), 4.10 (2H, $J=7.0$ Hz), Hz), 6.94 (2H, d, $J=8.0$ Hz), 7.12 (2H, d, $J=8.0$ Hz), 7.32 (1H, t, $J=8.0$ Hz), 7.37 (2H, d, $J=9.0$ Hz), 7.87 (1H, d, $J=8.0$ Hz), 8.23 (1H, d, $J=8.0$ Hz), and 8.30 (2H, d, $J=9.0$ Hz) ppm.

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