Synthesis and Thermal Properties of Nematic Liquid Crystalline Compounds Having a Coumarin Skeleton at the Terminal Position

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Homologous series of 2-oxo-2*H*-chromen-6-yl 6-alkoxynaphthalene-2-carboxylate (compounds 1) were synthesized and their mesomorphic properties were studied. Compounds 1 showed a nematic (N) phase on cooling process. The isotropic (I)- N transition temperatures of these compounds were estimated to be ca. 140°C on average. We calculated optimized structures of the liquid crystal cores of compounds 1, corresponding benzoate derivatives (compounds 2), and biphenyl-carboxylate derivatives (compounds 3), and found that the N-I transition temperatures seem to have a linear correlation with the core length/width ratio of compounds 1-3. We conclude that the geometrical anisotropy is one of the important factors for the N-I transition temperatures.
Key words: Coumarin derivatives, Synthesis, Liquid crystals, Nematic-Isotropic temperatures, Molecular structure

1. INTRODUCTION

It has been well known that mesomorphic and electro-chemical properties of liquid crystal materials entirely depend on their molecular structures.[1] Especially, the terminal polar group of the liquid crystal materials could modify a dielectric anisotropy as well as phase transition temperatures. A positive dielectric anisotropy is one of the very important factors to achieve low power consumption on twisted nematic mode display applications as follows. [2]

The threshold voltage (V_{th}) at which the first distortion of the director occurs is given by the equation (1): [3]

$$V_{th} = \pi \sqrt{\frac{k_{11}}{\varepsilon_0 \cdot \Delta\varepsilon}} \qquad (1)$$

k_{11}; splay elastic constant

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp},$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the dielectric constants measured parallel and perpendicular to the liquid crystal director and ε_0 =8.854 × 10^{-12} As/Vm, the dielectric constant of free space. The threshold voltage V_{th} is independent of the cell thickness and depends on the splay elastic constant k_{11} and the dielectric anisotropy $\Delta\varepsilon$.

Liquid crystal materials having a large positive dielectric anisotropy have been developed up to now. The terminal cyano group is one of the representative examples from a chemical structural point of view, because it has a large dipole moment as shown in Fig. 1.

Lactone compounds also expect to have a large dipole moment along to the carbonyl and ether oxygen moieties, while ester compounds (e. g. ethyl acetate) show a small dipole moment (μ_{obs}=1.78 Debye) as shown in Fig. 1.

In our previous papers [8]-[12], we reported that newly synthesized liquid crystal materials having a terminal lactone skeleton exhibited a smectic A (SmA) phase.

On the other hand, compounds 2 and 3 (see Fig. 2) entirely show a nematic phase, where the N-isotropic (I) phase transition temperatures are too low or too high for applying the twisted nematic mode display applications. [13]
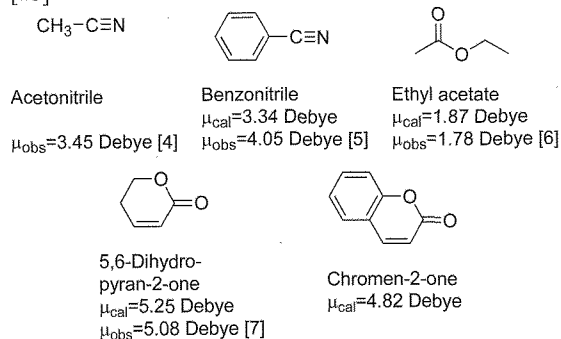

Fig. 1. Calculated (μ_{cal}) and observed (μ_{obs}) dipole moments for nitrile and carbonyl compounds. MOPAC AM1 method was used for semi-empirical molecular orbital calculations.
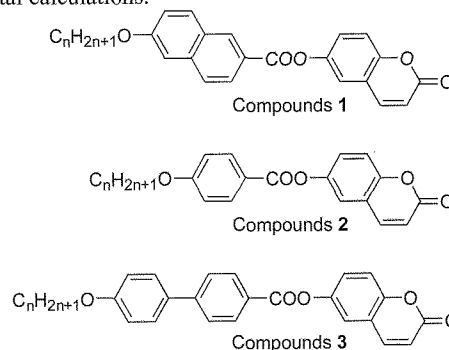

Fig. 2. Chemical structures of compounds 1-3.

In the present study, we newly synthesized homologous series of compounds **1** (see Fig. 2) and compared their thermal properties of homologous series with those of compounds **2** and **3**.

2. EXPERIMENTAL
2.1 Method

The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900). The transition temperatures were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard (mp=156.6°C). The DSC thermogram was operated at a heating or cooling rate of 5 K min^{-1}. ^{1}H NMR spectra were measured using a JEOL EX-270 spectrometer, where tetramethylsilane was used as an internal standard. IR spectra were recorded with a Shimadzu Prestige-21 infrared spectrometer. The purity of the materials was checked by HPLC. Semi-empirical molecular orbital calculations were achieved using CS Chem3D Pro and CS MOPAC Pro package, where AM1 method is used.

2.2 Materials

Homologous series for compounds **1** were prepared according to scheme 1 in a moderate yield. The chemical structures for compounds **1** including their intermediates are confirmed in terms of ^{1}H NMR and infrared spectroscopy. The purities of compounds **1** were checked with HPLC measurements (>99%).
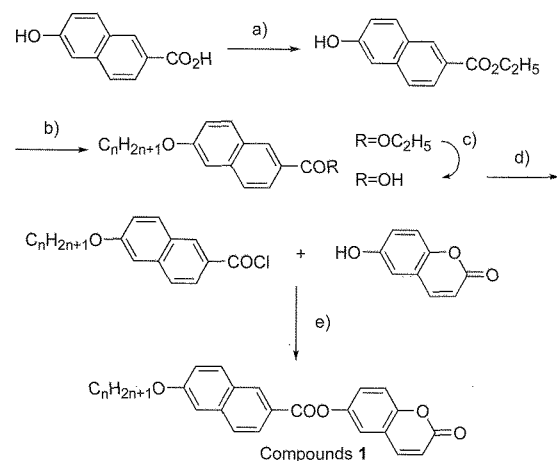
Scheme 1. Reagents and conditions: a) H_2SO_4, C_2H_5OH, reflux for 4 h, yield 85%; b) $C_nH_{2n+1}Br$, K_2CO_3, 3-pentanone, reflux for 24 h, yields 52-79%; c) aq.NaOH, DMSO, 3 h, then poured into 2N HCl, 71-93%; d) $SOCl_2$, 70°C, for 1 h, e) Pyridine, toluene, 80°C for 20 h, yields 60-70%.

Spectra data for butoxy homologue of compounds **1** is as follows; IR (KBr) υ=1190, 1719, 1742 and 2941 cm^{-1}, ^{1}H NMR (CDCl$_3$) δ=1.02 (3H, t, J=7.3 Hz), 1.57 (2H, six., J=7.6 Hz), 1.86 (2H, qui., J=6.7 Hz), 4.13 (2H, t, J=6.6 Hz), 6.48 (1H, d, J=9.6 Hz), 7.19 (1H, d, J=2.3 Hz), 7.23 (1H, dd, J=8.9, 2.3 Hz), 7.38-7.48 (3H, m), 7.70 (1H, d, J=9.8 Hz), 7.81 (1H, d, J=8.6 Hz), 7.88 (1H, d, J=8.9 Hz), 8.13 (1H, dd, J=8.6, 1.7 Hz), 8.69 (1H, d, J=1.3 Hz) ppm.

Synthetic schemes and spectra data for the homologous series of compounds **2** and **3** were shown in our previous paper [13].

3. RESULTS AND DISCUSSION

Thermal properties for compounds **1** were measured in terms of polarized microscope observations and differential scanning calorimeter.

Pentyloxy homologue of compounds **1**, for example, melted at 177°C with an endotherm on first heating process. On cooling process, schlieren texture was observed at 140°C in polarized microscope observation as shown in Fig. 3. Therefore, the mesophase for the pentyloxy homologue of compounds **1** is assigned to be a N phase.
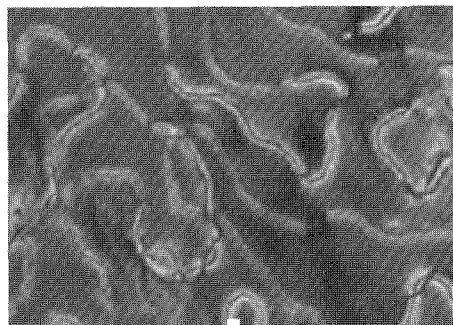

Fig. 3. Polarized micrograph of N phase (140°C) of pentyloxy homologue of compounds **1**.

The transition temperatures for compounds **1-3** are summarized in Table I-III. All the homologues for compounds **1** show the N phase on cooling process and the N-I transition temperatures decrease with increasing carbon number (n).

Compounds **2** also show a monotropic N phase for small-n homologues, while the hexyloxy homologue and large-n ones interestingly do not show any mesomorphic properties. The mesomorphic properties for the hexyloxy homologues and the latters estimated from the binary phase diagrams are shown in the Table II.

Table I. Transition temperatures of compounds **1**

Carbon number (n)	Transition temperature (°C)		
	C	N	I
4	• 168	(• 152)	•
5	• 177	(• 140)	•
6	• 167	(• 139)	•
7	• 159	(• 135)	•
8	• 165	(• 137)	•

C means crystal. Parentheses mean a monotropic transition.

Table II. Transition temperatures of compounds **2**

Carbon number (n)	Transition temperature (°C)		
	C	N	I
4	• 98	(• 78)	•
5	• 88	(• 78)	•
6	• 96	[• 80]	•
7	• 101	[• 84]	•
8	• 102	[• 88]	•

Brackets mean a virtual transition.

Table III. Transition temperatures of compounds **3**

Carbon	Transition temperature (°C)			
number (n)	C	SmA	N	I
5	• 155	–	• 249	•
6	• 96	–	• 240	•
7	• 102	–	• 239	•
8	• 102	• 208	• 232	•

SmA means smectic A phase.

Compounds **3** also show the N phase with high thermal stabilities and the octyloxy homologue exhibit SmA phase in addition.

The transition temperatures for compounds **1-3** are plotted against the carbon number (n) of the terminal alkyl chain as shown in Fig. 4-6. The N-I phase transition temperatures of compounds **1** slightly show an even-odd effect and the average of the N-I phase transition temperatures is estimated to be ca. 140°C. Those of compounds **2** and **3** are ca. 90°C and 240°C, respectively.
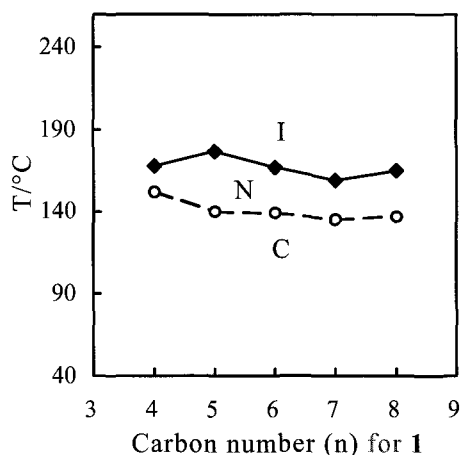
Fig. 4.   Plots of transition temperatures (°C) vs. the carbon number (n) of compounds **1**.
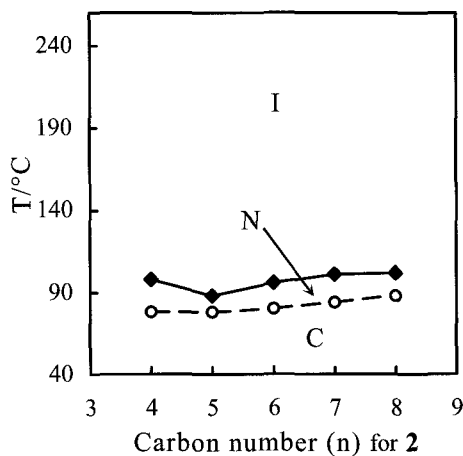
Fig. 5.   Plots of transition temperatures (°C) vs. the carbon number (n) of compounds **2**.
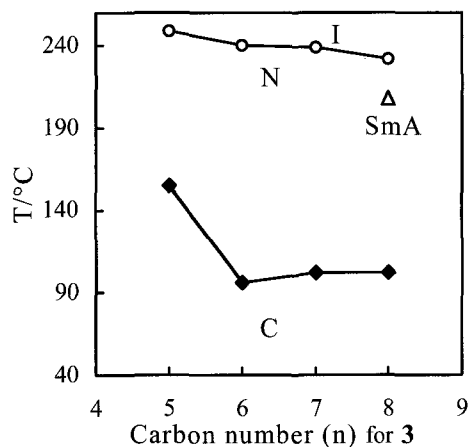
Fig. 6.   Plots of transition temperatures (°C) vs. the carbon number (n) of compounds **3**.

It is well known that the N-I phase transition temperatures have a correlation with geometrical anisotropy of the liquid crystal core, so that the liquid crystal core structures without the terminal 2-oxo-chromen-2-one of compounds **1-3** are calculated using semi-empirical molecular orbital calculations and the results are shown in Fig. 7.
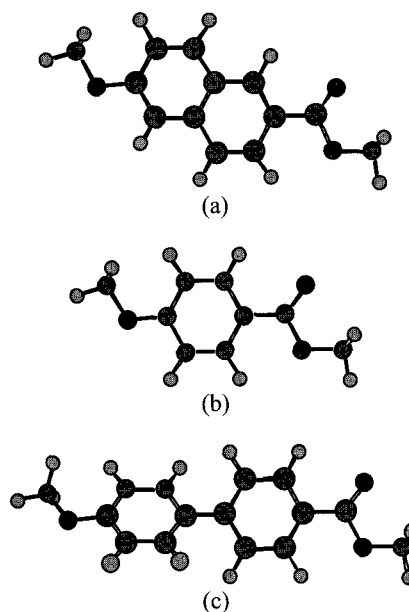
Fig. 7.   Liquid crystal core structures of (a) compounds **1**, (b) compounds **2**, and (c) compounds **3**, optimized with semi-empirical molecular orbital calculations (MOPAC).

The three dimensions (length, width and depth) of the liquid crystal core of compounds **1-3**, and their core length/width ratio are also summarized in Table IV. The core structures of compounds **1** and **2** are planar, so the depth of the core is 1.8 Å, while that of compounds **3** having twisted two benzene rings is 2.4 Å. The width of the core of compounds **1** was calculated to be 5.4 Å, while those of compounds **2** and **3** are the same. The core lengths of compounds **1-3** were also calculated to

be 12.3, 10.2 and 14.3 Å, respectively. Therefore, the length/width (L/W) ratios of compounds **1-3** were calculated to be 2.3, 2.1 and 2.9, respectively.

Table IV. Molecular dimensions of liquid crystal core of compounds **1-3**

	L (Å)	W (Å)	D (Å)	L/W
Compounds **1**	12.6	5.4	1.8	2.3
Compounds **2**	10.2	4.9	1.8	2.1
Compounds **3**	14.3	4.9	2.4	2.9

L, W, and D mean length, width, and depth of liquid crystal core of compounds **1-3**, respectively.

The N-I transition temperatures of compounds **1-3** are plotted against the L/W ratio as shown in Fig. 8. The N-I transition temperatures seem to have a linear correlation with the L/W ratio. Thus we concluded that the geometrical anisotropy is one of the important factors for the N-I transition temperatures.

The research on the relation between the chemical structures and mesomorphic properties is now progressing, and the results will be published elsewhere.
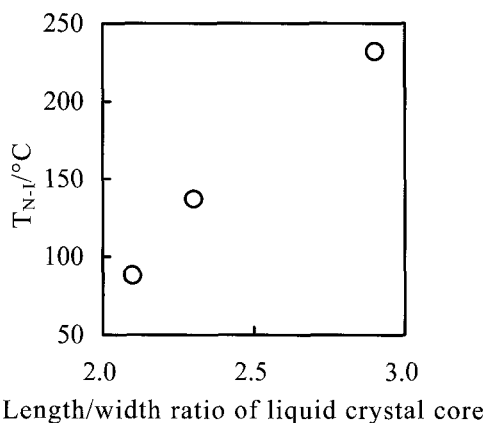
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Fig. 8. N-I transition temperatures vs. the core length/width ratio of compounds **1-3**.

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