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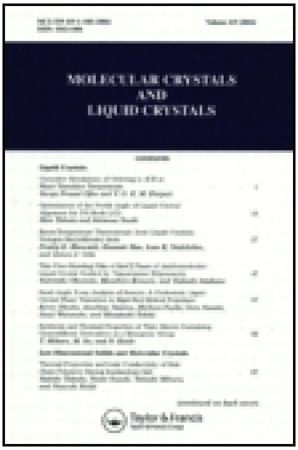

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Liquid Crystalline Properties of Some Derivatives with a Long Lateral Alkoxyl Group

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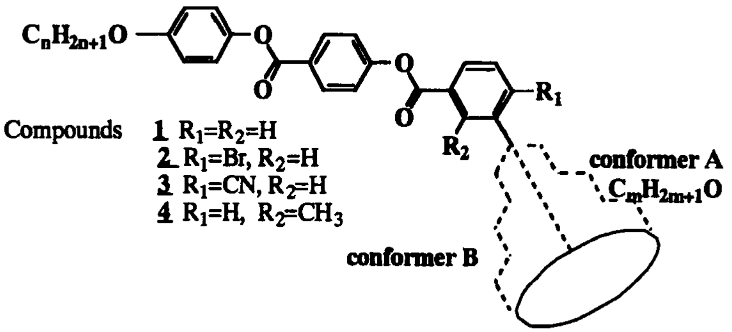
This paper describes the liquid crystalline properties of 4-(4-alkoxy-phenoxycarbonyl)phenyl 4-bromo-3-alkoxy-(**2**),4-cyano-3-alkoxybenzoates(**3**), and 2-methyl-3-alkoxybenzoates(**4**). **2** and **3** are essentially smectogenic, while **4** are nematogenic. The difference in the mesomorphic properties is discussed in terms of their molecular geometrical characteristics estimated by a semi-empirical molecular orbital calculation.

Keywords: liquid crystals; substituent effect; Smectic C; thermal property; conformational analysis

INTRODUCTION

Generally, rod-like liquid crystals have a long alkyl chain(s) at one and/or both terminal positions, in order to increase linearity and flexibility of the entire molecular shape. On the other hand, the long alkyl group introduced at the lateral position is not preferable for liquid crystallinity,[1-3] since it increases the molecular breadth, or bends the entire molecular shape. The typical example is shown below. These compounds have a long alkoxy chain at the meta



Compounds
1 $R_1=R_2=H$
2 $R_1=Br, R_2=H$
3 $R_1=CN, R_2=H$
4 $R_1=H, R_2=CH_3$

position to the ester group. The alkoxy chain would rotate almost freely, and give two extreme conformers, **A** and **B**. As we can see from the figure, conformer **A** should keep the good linearity of the entire molecular shape, while **B** would result in a notable bent, and be unfavorable for liquid crystalline properties. However, these two conformers are equivalent in point of energy, so that population of two conformers is equivalent in gas and liquid phases, of course, in liquid crystal one. If $\mathbf{R_1}$ or $\mathbf{R_2}$ can restrict the rotation of the alkoxyl group, then these compounds are expected to show a certain liquid crystalline state. Under the assumption, we prepared some derivatives of **1** – **4**, and examined the physicochemical properties.

EXPERIMENTALS

Derivatives of **1** – **4** were prepared by a conventional method appeared in our earlier paper.[4] The transition temperatures and latent heats were determined using a Seiko SSC-5200 DSC, where indium (99.9%) was used as a calibration standard. The mesophases were characterized using a Nikon POH polarizing microscope fitted with a Mettler thermo-control system (FP-900).

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RESULTS AND DISCUSSION

The transition temperatures and latent heats for the derivatives are summarized in TABLE 1.

TABLE 1 Transition temperatures (T/°C) and latent heats (kJ/mol) for **1** – **4**

Compounds					Transition temperatures									Latent heats		
	m	n	R_1	R_2	C		Sm C		Sm A		N		I	ΔH_1	ΔH_2	ΔH_3
1a	2	5	H	H	•	98	-		-		-		•			
1b	5	5			•	76	-		-		-		•			
2a	2	5	Br	H	•	111	-		(•	91	•	100)	•	0.0	0.3	0.7
2b	5	5			•	96	(•	70	•	83	•	84)	•	0.3	2.2	0.3
2c	8	6			•	73	•	82	•	96	-		•	0.0	3.0	
3a	2	5	CN	H	•	137	-		-		•	143	•			0.6
3b	5	5			•	112	(•	104)	-		•	114	•	3.9		0.7
3c	10	6			•	101	•	124	-		-		•	8.2		
4a	6	6	H	CH_3	•	77	-		-		•	83	•			0.5
4b	14	6			•	81	-		-		(•	75)	•			0.6
4c	14	8			•	81	-		-		(•	74)	•			0.7

Parenthesis indicates a monotropic transition. ΔH_1 ,ΔH_2, and ΔH_3 indicate the latent heats for Sm C-Sm A (N), Sm A-N, and N-I transitions, respectively.

The homologous series of **1** have been known to be poor in mesomorphic properties.[1] In fact, **1a** and **1b** do not show any mesophase even in the rapid cooling of the isotropic solution. For homologous series of **2**, the members (m=1, 2) show the phase sequence of a (Sm A)-N-I type. The members (m>5) shown in TABLE 1 tend to show the phase sequence of a Sm C-Sm A-N-I type, and Sm A and N ranges become narrow with increasing m. The members with m=14, for example, predominantly have the phase sequence of a Sm C-I type.

For the homologous series of **3**, the members (m>3) have the phase sequence of a Sm C-N-I type, and formation of the Sm C phase becomes predominant with increasing m.[4] As shown in TABLE 1, the Sm C phase is formed even in the members with m=14.

For the homologous series of **4**, interestingly, the members with m=6 or 14 exhibit only a N phase having an ordinal schlieren texture.

These results indicate that the substituent adjacent to the alkoxyl group is important in determining the mesomorphic pathway of the present system. In order to find the correlation between mesomorphic properties of four systems and molecular structures, some binary phase diagrams were examined, and the results are shown in Figures 1 and 2.

In Figure 1, **1b** has a virtual N-I transition temperature around 20 °C, which is lower by more than 200 °C compared with the corresponding para-substituted derivative.[1] In the mixture of **2b** and **3b** N and Sm C phases of both components are miscible each other, though the Sm A-N transition temperature shows an upward convexity,

In Figure 2, on the other hand, Sm C-Sm A and Sm A-N transitions of **2b** steeply decrease around the center of the diagram, and the N-I transition temperature shows non-linear behavior, indicating that both **4** and **2** have different mesomorphic properties, probably due to large difference in their molecular shapes. For the mixture of **4a** and **5**, Sm C-N and N-I transition temperatures show a linear correlation against the molar concentration. Furthermore, the Sm C-N transition becomes ambiguous, and disappears around 70 mol % of **5**. These results indicate that these two molecules are miscible each other in the mesophases. These mesomorphic characteristics are understood by correlation of rotational barrier and torsional angle, as shown in Figure 3.

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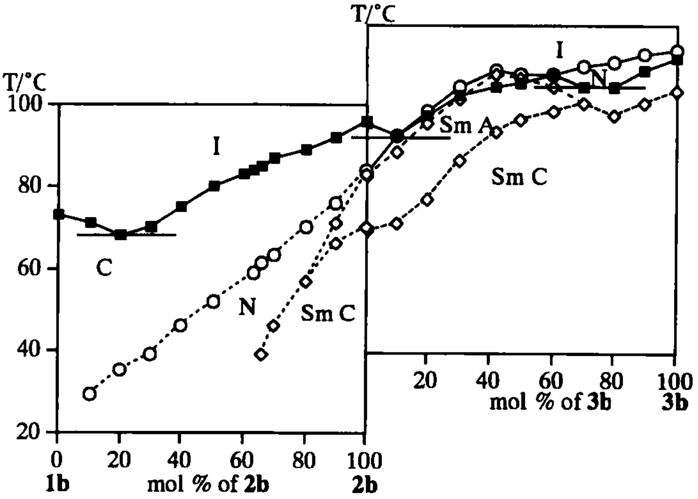

FIGURE 1. Phase diagrams for the mixtures of **1b** and **2b** (on left) and **2b** and **3b** (on right).

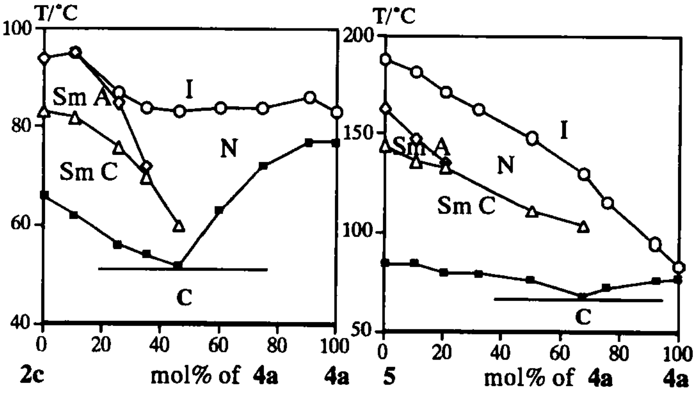

FIGURE 2. Phase diagrams for the mixtures of **2c** and **4a** (on left) and **4a** and 4-octyloxyphenyl 4-(4-octyloxybenzoyloxy)benzoate,**5** (on right).

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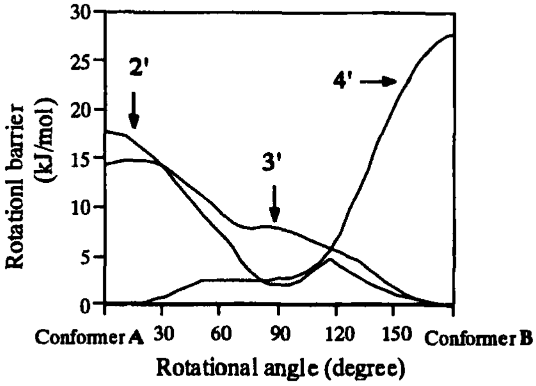

FIGURE 3 Rotational barriers for methyl 4-bromo(2'), 4-cyano(3'), 2-methyl(4')-3-ethoxybenzoates calculated by AM1 method (MOPAC).

As we can see from Figure 3, **2** and **3** are intrinsically bent molecules (conformer **B**), while **4** are linear one (conformer A), due to steric hindrance between the alkoxyl group and the adjacent substituents. For **1**, rotation around the phenyl-O-alkyl bond gives the mixture of linear and bent shapes (A+**B**), resulting in the low mesomorphic properties. This geometrical difference should be mainly responsible for the characteristic mesomorphic pathways for these four systems.

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