A New Series of Liquid Crystals Having a Terminal Carbonyl Group

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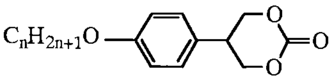
Some homologs of 5-(4-alkoxyphenyl)-1,3-dioxan-2-one exhibit a monotropic smectic A phase commencing from the pentyloxy homolog.

Dielectric anisotropy is one of the important physical parameters of liquid crystal materials for display device. Positive dielectric anisotropy is an inevitable requisite for the materials for the TN mode. The dielectric properties are arised from the dipole moment of polar functional groups within the molecules. Therefore, a lot of liquid crystals having a terminal polar group such as a cyano group or a nitro one have been extensively developed.[1]

It has been well known that a carbonate group also has a large dipole moment compared with the cyano and nitro ones. Thus, we examined the effectiveness of a 1,3-dioxan-2-one core as a composite of liquid crystal molecule. This paper describes the synthesis and thermal properties of 5-(4-alkoxyphenyl)-1,3-dioxan-2-one, shown below.



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Compounds **1** were prepared according to Scheme, and the purity was checked by an elementary analysis. The chemical structures were confirmed by ^{1}H NMR and IR spectroscopies.[2]

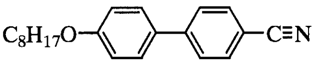
The transition temperatures and the latent heats were determined using a Seiko SSC-5200 differential scanning calorimeter (DSC), where the apparatus was operated at a heating or a cooling rate of 5 °C/min. The results are summarized in Table 1, where the the isotropic(I)–mesophase(M) transition was determined from the cooling process. The mesophase with a focal conic fan texture commences from the pentyloxy homolog, and the transition temperature increases on ascending the homolog. The mesophase was characterized from the consideration of binary phase diagrams, shown in Figure 1.

Table 1. Transition temperatures (T/ °C) and latent heats (kJ/mol) for compounds **1**

Compounds	n	C		M		I	$\Delta H_{C\text{-}I}$	$\Delta H_{M\text{-}I}$
1a	3	•	100	-		•	27.6	
1b	4	•	86	-		•	27.3	
1c	5	•	60(	•	12)	•	30.2	0.8
1d	6	•	61(	•	39)	•	23.7	1.6

C, M, and I indicate crystal, mesophase, and isotropic phases respectively. Parentheses indicate a monotropic transition.

The smectic phase was further characterized by phase diagrams for the mixture of **1c** and polar and nonpolar liquid crystals. In Figure 1a, the smectic phase of **1c** is miscible with the smectic Ad phase of **2**, and the smectic–nematic(isotropic) transition temperature shows a linear correlation with the concentration of each component. In the mixtures of nonpolar liquid crystals, **3** and **4** (Figures 1b and 1c), the smectic–nematic (isotropic) transition temperatures show a typical phase behavior frequently observed in polar-nonpolar liquid crystal mixtures.[4] The characteristic behavior suggests that the smectic phase of **1c** is the A modification(Sm A) with a polar nature similar to that of **2**. The Sm A-I transition temperature for the binary mixture of **1d** and **2** shows a similar behavior.



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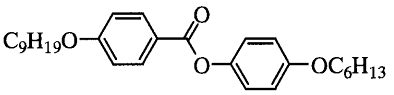

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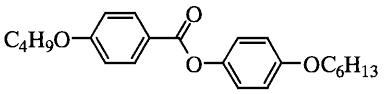

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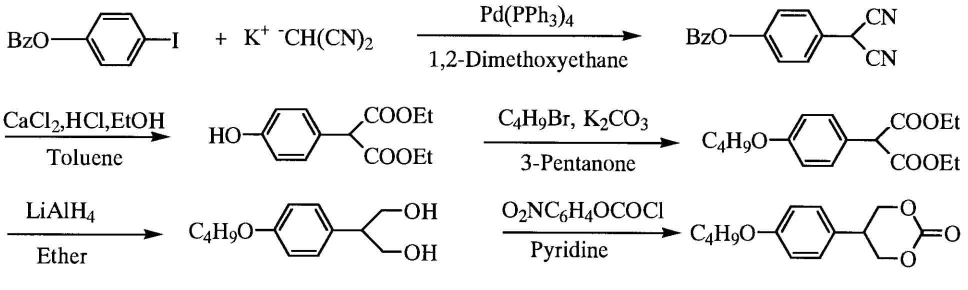
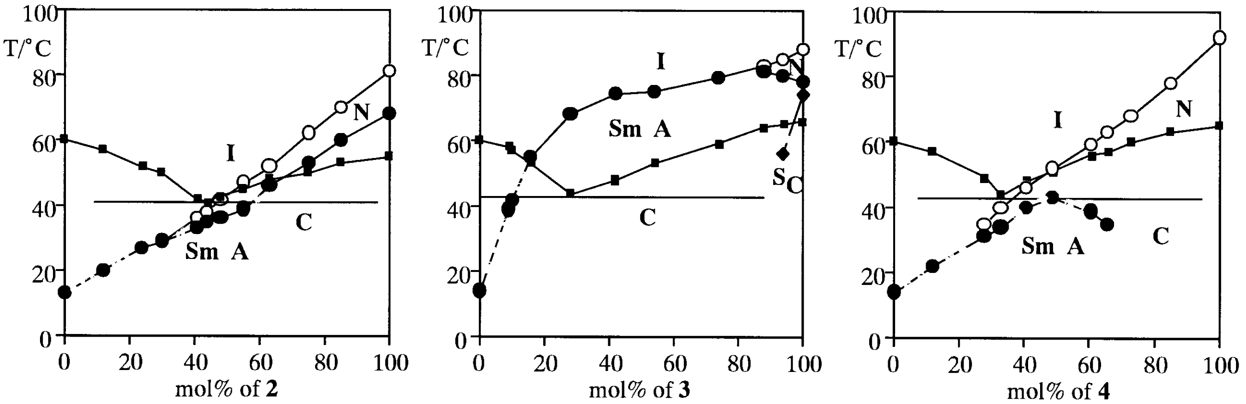
It has been known that 1,3-dioxane[5] and 1,3-dithiane[6] cores are important constituents for liquid crystal materials. However, the core would be poor in polarity. On the other



Scheme 1. Bz = benzyl group



(a) (b) (c)

Figure 1. Binary phase diagrams for the mixtures: (a); **1c** and 4-octyloxy-4'-cyanobiphenyl(**2**), (b); **1c** and 4-hexyloxyphenyl 4-nonyloxybenozoate(**3**)[3], and (c); **1c** and 4-hexyloxyphenyl 4-butoxybenzoate(**4**)[3] Labels ■, ◆, ●, and ○ indicate crystal- nematic(N), Sm A, or I, Smectic C-Sm A, Sm A-N or I, and N-I transitions, respectively. Dashed lines indicate a monotropic transition.

hand, the 1,3-dioxan-2-one is expected to have a large dipole moment, due to the –O–CO–O– group. In fact, the dipole moment calculated by a semi-empirical molecular orbital calculation (CS MOPAC ver. 6.0) is 7.21 D for **1c**, where the most stable conformation at 25 °C for single molecule was calculated by an AM1 method.

A similar calculation for **2** gives the dipole moment of 4.67 D. Therefore, we can expect that compounds **1** have a large dielectric anisotropy similar to **2**. The dielectric anisotropy for **1c** determined in commercial liquid crystal mixture (3.0 w/w% in ZLI-4792 ($\Delta\varepsilon$ = 1.2(our observation), Merck) was 2.8 at 25 °C.

Further examination is now underway.

References

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2 **1c**: Anal. Found: C, 68.00 %; H, 7.55%. Calcd for $C_{15}H_{20}O_4$: C, 68.16 %; H, 7.63%. ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.93 (3H, t, *J* = 7.1 Hz), 1.31–1.49 (4H, m), 1.78 (2H, qui, *J* = 6.9 Hz), 3.44 (1H, tt, *J* = 10.2, 5.3 Hz), 3.94 (2H, t, *J* = 6.6 Hz), 4.47 (2H, t, *J* = 10.2 Hz, 4.53 (2H, dd, *J* = 10.2, 5.3 Hz), 6.90 (2H, d, *J* = 8.9 Hz), 7.13(2H, d, *J* = 8.9 Hz) ppm. IR (KBr disc): ν = 1729 cm^{-1} (ν_{CO}). The large coupling constant of the methine proton at 3.44 ppm indicates that the methine proton is substituted at the axial position of 1,3-dioxan-2-one. Therefore, it is assumed that the 1,3-dioxan-2-one core has a half-chaiar form. In this connection, it has been reported that in 4-substituted cyclohexanone systems, the axial conformation with a chair form is predominant. (R. D. Stolow, T. Groom, and P. D. McMaster, *Tetrahedron Lett.*, **1968**, 5781.)

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