RAPID PAPER

Synthesis and Properties of Cholesteryl Benzoate Derivatives: Liquid Crystals and Organogelators

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Edited by M. Toyota, Tokushima Bunri Univ., and accepted July 1, 2004 (received for review May 27, 2004)

Abstract: New liquid crystals and organogelators with a cholesteryl benzoate skeleton were prepared. Cholesteryl 4-alkoxy- and 3,4-dialkoxybenzoates had enantiotropic cholesteric and smectic A phases, while 3,5-dialkoxy- and 3,4,5-trialkoxybenzoate derivatives were not mesomorphic. Furthermore cholesteryl 4-alkoxy- and 3,4-dialkoxybenzoates gelled organic solvents such as 1-decanol and n-hexadecane.

Key words: liquid crystal, organogelator, smectic A phase, cholesteric phase, cholesteryl benzoate

1 Introduction

Self-assembled systems such as gelators and liquid crystals receive much attention from both theoretical and practical viewpoints. Numerous studies have been dedicated to the structural investigation to the determination of the molecular aggregation mechanisms. The number of known organogelators and liquid crystals has increased dramatically in recent years. However, the numbers (ca. 100 molecules) of low-mass organogelators (1-3) is fewer than that (ca. 82000 molecules) of liquid crystals (4). In these molecules, some molecules have mesomorphic and organogelation properties. For example, the mesomorphic and organogelation properties of octa-alkoxy substituted β -diketonato copper complex (5), octa(dodecyl)tetrapyrazinoporphyrazine (6), 3,4,5-trialkoxybenzoylamines (7), 2-(3,4,5-trialkoxybenzoylamino)-5-cyanotropones (8), and 2,2'-

di(3,4,5-trialkoxybenzoylamino)-5,5'-bitropones (9) etc. are reported. We named such molecule 'organogelling liquid crystals' (10). As a study of new organogelling liquid crystals, we report the mesomorphic and gelation properties of cholesterol derivatives (**1-4**) having 4-alkoxybenzoyl group (11), 3,4-dialkoxybenzoyl group, 3,5-dialkoxybenzoyl group, and 3,4,5-trialkoxybenzoyl group.

2 Experimental

The synthetic details and physical properties of **1-4** will be reported elsewhere. The results of the elemental analyses are as follows. **1a** (46%); Anal. Found: C, 81.28; H, 10.67%. Calcd for C₄₀H₆₂O₃: C, 81.30; H, 10.58%. Found: C, 81.59; H, 10.91%. **1b** (59%); Anal. Calcd for C₄₄H₇₀O₃: C, 81.68; H, 10.90%. Found: C, 81.80; H, 11.20%. **1c** (44%); Anal. Calcd for

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Scheme

$C_{48}H_{78}O_3$: C, 81.99; H, 11.18%. **2a** (66%); Anal. Found: C, 79.86; H, 10.83%. Calcd for $C_{46}H_{74}O_4$: C, 79.95; H, 10.79%. **2b** (53%); Anal. Found: C, 80.63; H, 11.28%. Calcd for $C_{54}H_{90}O_4$: C, 80.74; H, 11.29%. **2c** (82%); Anal. Found: C, 81.09; H, 11.70%. Calcd for $C_{62}H_{106}O_4$: C, 81.34; H, 11.67%. **3a** (88%); Anal. Found: C, 79.78; H, 10.76%. Calcd for $C_{46}H_{74}O_4$: C, 79.95; H, 10.79%. **3b** (45%); Anal. Found: C, 80.55; H, 11.20%. Calcd for $C_{54}H_{90}O_4$: C, 80.74; H, 11.29%. Anal. **3c** (52%); Anal. Found: C, 81.16; H, 11.68%. Calcd for $C_{62}H_{106}O_5$: C, 81.34; H, 11.67%. **4a** (82%); Anal. Found: C, 78.75; H, 10.94%. Calcd for $C_{52}H_{86}O_5$: C, 78.93; H, 10.96%. **4b** (65%); Anal. Found: C, 80.07; H, 11.47%. Calcd for $C_{64}H_{110}O_5$: C, 80.11; H, 11.55%. **4c** (51%); Anal. Found: C, 80.66; H, 11.90%. Calcd for $C_{76}H_{134}O_5$: C, 80.93; H, 11.98%.

The transition temperatures were measured by differential scanning calorimetry (Seiko DSC 6200) and the mesomorphic phases were observed by polarizing optical microscopy (Olympus BHSP BH-2 equipped with a

Linkam TH-600MS hot stage). X-ray diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-K α radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

3 Results and Discussion

3.1 Synthesis of Troponoid Compounds

Cholesteryl benzoate derivatives (**1-4**) were prepared by the esterification of cholesterol with the corresponding benzoic acid derivative in the presence of EDC·HCl and DMAP. The structure and purity of the compounds (**1-4**) were ascertained by NMR spectroscopy, FAB MS and elemental analysis.

3.2 Mesomorphic and Gelation Properties

The transition temperature and thermal behaviors of the compounds (**1-4**) were determined using a differential scanning calorimeter and a polarizing microscope equipped with a hot stage as well as an X-ray diffraction study. Optical micrograph of **2a** are shown in **Fig. 1**. The smectic A and cholesteric phases were determined from a following observation as well as an X-ray diffraction study, i.e., focal-conic fan, and homeotropic textures for the smectic A phase; Gandjean steps at the border and oily streak textures for the cholesteric phase. The thermal behaviors of the cholesteryl benzoates are summarized in **Table 1**. Cholesteryl 4-alkoxybenzoates (**1**) and 3,4-dialkoxybenzoates (**2**) had a phase sequence of crystal-smectic A - cholesteric - isotropic, while the

Fig. 1 Optical Cross-Polarising Microscopy Photographs of **2a** at (a) 80°C (SmA) and (b) at 110°C (N*). All pictures taken on cooling from the isotropic phase.

Table 1 Transition Temperatures ($^{\circ}\text{C}$) and Transition Enthalpies ($\text{kJ}\cdot\text{mol}^{-1}$) of **1-4**.

Compound	Transition temperatures / $^{\circ}\text{C}$ (Transition enthalpies / $\text{kJ}\cdot\text{mol}^{-1}$)
1a	Cr·150.9 (13.3)·N*·229.9 (0.8)·Iso
1b	Cr·110.4 (35.5)·SmA·177.7 (0.7)·N*·208.1 (1.0)·Iso
1c	Cr·117.6 (18.2)·SmA·175.9 (0.7)·N*·190.2 (0.8)·Iso
2a	Cr·90.6 (13.3)·SmA·99.4 (0.3)·N*·116.8 (0.4)·Iso
2b	Cr·73.4 (15.1)·SmA·90.3 (0.8)·N*·98.1 (0.6)·Iso
2c	Cr·61.4 (12.8)·SmA·73.4 (0.3)·N*·84.1 (0.4)·Iso
3a	Cr·57.5 (57.5)·Iso
3b	-
3c	-
4a	Cr·52.9 (16.5)·Iso
4b	Cr·42.6 (39.6)·Iso
4c	Cr·25.7 (36.8)·Iso

Cr: Crystals, SmA: Smectic A Phase, N*: Cholesteric Phase, Iso: Isotropic Liquid.

Fig. 2 Photograph of **1a**-1-decanol Gel (3.6 wt%).

cholesteryl 3,5-dialkoxybenzoates (**3**) and 3,4,5-trialkoxybenzoates (**4**) were not mesomorphic. The melting and clearing points of **2** were lower than those of the cholesteryl 4-alkoxybenzoates (**1**).

Furthermore, we employed the gelation test of **1-4** in various organic solvents as shown in **Table 2**. **Figure 2** shows a photograph of the gel of **1a** in 1-decanol (3.6 wt%) taken at 25°C on cooling from an isotropic liquid state. Interestingly, the mesomorphic compounds **1** and **2** gelled organic solvents such as 1-decanol and hexadecane, while non-mesomorphic compounds were not organogelator.

3.3 X-Ray Diffraction Analysis

We measured the X-ray diffraction pattern of the mesophases. The smectic layer spacings (d) and molecular lengths (l) of **1** and **2** were shown in **Table 3**. The

Table 2 Gelation Test of **1-4**.

Solvent	1a	1b	1c	2a	2b	2c	3a	4a	4b	4c
Hexane	Cr	Cr	Cr	Sol	Sol	Sol	Sol	Sol	Sol	Sol
<i>n</i> -Decane	Cr	Cr	Cr	Sol	Sol	Sol	Sol	Sol	Sol	Sol
<i>n</i> -Hexadecane	Gel	Gel	Gel	Sol	Sol	Gel	Sol	Sol	Sol	Sol
Methanol	Insol	Insol	Insol	Cr	Cr	Cr	Cr	Cr	Cr	Cr
Ethanol	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr
1-Decanol	Gel	Gel	Gel	Gel	Gel	Gel	Sol	Sol	Sol	Sol
Ethyl acetate	Cr	Cr	Cr	Sol	Sol	Cr	Sol	Sol	Sol	Sol
Acetonitrile	Insol	Insol	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr
Tetrahydrofuran	Cr	Sol	Sol	Sol	Sol	Sol	Sol	Sol	Sol	Sol

Cr: Crystallization, Sol: Solution, Insol: Insoluble, Gel: Gelation, 100mg **1-4** / 1mL Solvent

Table 3 Layer Spacings (Å) and Molecular Lengths (Å) of **1** and **2**.

Compound	X-Ray diffraction		MM2 calculation
	Temp. / °C	Layer spacings / Å	Molecular lengths / Å
1b	120	32.6	36.4
1c	120	36.8	41.4
2a	95	30.7	31.4
2b	77	34.8	36.4
2c	68	38.9	41.4

Fig. 3 Packing Model of **2b** in the Smectic A Phase and Molecular Structure of **2b** Generated by MM2 Calculation.

molecular lengths (l) of **1** and **2** were calculated by MM2 method. The d/l ratio of the smectic A phase of **1** and **2** are 0.87-0.98. This result suggests that **1** and **2** are arranged with their molecular long axes perpendicular to the planes of the layer in the smectic A phase (12) and form the layer as shown in **Fig. 3**. Although Vill and Thiem (11) have been reported that compounds **1b** and **1c** had monotropic smectic C phase, the change of the layer spacings of **1b** and **1c** corresponding to SmA-SmC phase transition at each temperature has not been observed.

4 Conclusion

Cholesteryl 4-alkoxy- and 3,4-dialkoxybenzoates (**1,2**) had mesomorphic and organogelation properties.

Compounds (**1,2**) would be classified into organogelling liquid crystals. From now on, many organogelling liquid crystals will be found in the research of new organogelator and liquid crystals.

Acknowledgements

This work was supported by the funds from Fuji Photo Film Co. Ltd and Ministry of Education, Science, Sports and Culture of Japan.

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