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Phase transitions of 6-(4-*n*-alkoxybenzoyloxy)-flavones and 3-cyano-7-(4-*n*-alkoxybenzoyloxy)-coumarins

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Phase transitions of 6-(4-*n*-alkoxybenzoyloxy)-flavones (ABF) and 3-cyano-7-(4-*n*-alkoxybenzoyloxy)-coumarins (CABC) were studied using D.S.C. and polarized microscopy. ABF series showed a nematic phase which has an excellent thermal stability, whereas CABC series exhibited a smectic A phase in the longer 4-*n*-alkoxybenzoyloxy ones than 4-*n*-hexyloxybenzoyloxy. This difference in the mesogenicity was discussed from the structure and polarity of flavone and coumarin skeletons which may be associated with an intermolecular interaction in the mesophase.

1. Introduction

Developments of new liquid crystal-forming compounds are always important to advance our understanding in physical properties of mesophase and to search for new functional mesomorphic materials. Our present interest on new mesomorphic compounds is focussed on flavone and coumarin derivatives. Flavone and coumarin derivatives are known to exist in vacuoles of epidermal cells of the petals in various natural plants, having a role of pigments in the textures, frequently by attaching to anthocyanin [1]. Since most of mediums in the vacuoles may be in liquid-crystalline state, it is interesting to study mesomorphic properties of flavone and coumarin derivatives. Mesogenicity of coumarin derivatives has been studied by a few researchers. Nakai *et al.* [2] first studied several coumarin derivatives. They found the presence of liquid crystalline phase in several 3,7-substituted coumarin derivatives as shown in figure 1. The type of mesophase depended on the chemical structure of groups substituted at the 3-position. Substitution of an alkoxy carbonyl group tends to produce smectic A phase, while a cyano group causes appearance of nematic phase besides the smectic A phase. Anisimova *et al.* [3] reported that 3-(4-ethoxyphenyl)-7-alkoxycoumarins show both smectic and nematic phases.

The flavone skeleton differs from the coumarin skeleton only in the position of C=O, as shown in figure 1. The difference in the position of C=O should change the structural and polar nature of the skeleton. However, no paper on the mesomorphic property of flavone derivatives has not been published, to our knowledge. It is of interest how the chemical structures of flavone and coumarin skeletons affect the mesomorphic property.

This paper describes phase transitions of 6-(4-*n*-alkoxybenzoyloxy)-flavones (ABF) and of 3-cyano-7-(4-*n*-alkoxybenzoyloxy)-coumarins (CABC). The difference in the mesogenicity between ABF and CABC was discussed.

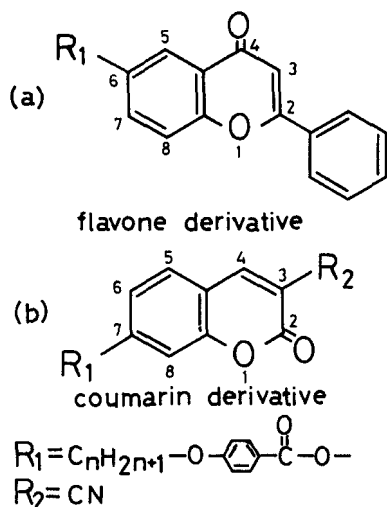


Figure 1. Chemical structure of flavone and coumarin derivatives.

2. Experimental

2.1. Materials

General syntheses of ABF: 2,5-Dihydroxyacetophenone(I) was prepared from hydroquinone diacetate and AlCl_3 by a conventional method [4]. 6-Hydroxyflavanone(II) was synthesized according to the method of Shah and Shah [5]; benzaldehyde (7 g, 0.066 mol)/ethanol (20 ml) solution was added to 2,5-dihydroxyacetophenone(I) (9 g, 0.059 mol) in the mixture of ethanol (300 ml) and 40 per cent NaOH (60 ml) in an ice bath, and stirred at room temperature for 4 days. The crude 6-hydroxyflavanone(II) crystals were precipitated by adding dilute HCl (2000 ml) to the reaction mixture. The crystals were filtered off and washed with chloroform, giving compound II as colourless powder in 23 per cent yield (3.2 g), m.p. = 220–222°C. 6-Methoxyflavanone(III) was prepared by stirring the mixture of 6-hydroxyflavanone(II) (6 g, 0.025 mol) in 1.5 N NaOH (80 ml) and dimethyl sulphate (12.5 g, 0.1 mol) for 30 min. The crude sample was purified by several recrystallizations from ethanol, to give compound III as colourless plate in 35 per cent yield (2.2 g), m.p. = 139 – 140°C. 6-Methoxyflavone(IV) was synthesized by the method of Takeno *et al.* [6]; 2-Pyrrolidone hydrogen tribromide (PHT) (5 g, 5.0 mmol) in DMSO (50 ml) was added to the solution of 6-methoxyflavanone(III) (1.2 g, 4.7 mmol) in DMSO (50 ml) by stirring at room temperature, and kept at 80°C for 3 h. After cooling to room temperature, water was added to the reaction mixture. The mixture was extracted with benzene, washed with brine, dried by anhydrous sodium sulfate and evaporated. The crude 6-methoxyflavone(IV) crystals obtained were purified by recrystallizations from ethanol, giving compound IV as colorless needles in 73 per cent yield (0.87 g), m.p. = 163 – 164°C. 6-Hydroxyflavone(V) was obtained by refluxing the mixture of 6-methoxyflavone(IV) (2.7 g, 0.011 mol) in acetic acid (100 ml) and 47 per cent HBr (20 ml) for 12 h. The crude crystals precipitated by adding water (500 ml) were washed with benzene and purified by recrystallizations from ethanol, giving compound V as yellow prisms in 51 per cent yield (1.32 g), m.p. = 230 – 231°C. Compound V; $^1\text{H-N.M.R.}$ (d_6 – DMSO): δ = 6.97(1H, s, C3–H), 7.30(1H, dd, C7–H), 7.35(1H, d, C5–H), 7.60(3H, m, 2-phenyl), 7.68(1H, d, C8–H), 8.10(2H, m, 2-phenyl), 10.03(1H, s, OH).

Finally, ABF's were prepared by a conventional dehydrochloride reaction of 6-hydroxyflavone(V) and 4-*n*-alkoxybenzoyl chloride in the mixture of benzene and pyridine. The crude crystals were fully purified by several recrystallizations from acetone. The crystals obtained were identified as ABF, using I.R., N.M.R. and MS: For example, ABF($n = 3$); $^1\text{H-N.M.R.}(\text{CDCl}_3)$: $\delta = 1.09(3\text{H, t, CH}_3)$, $1.88(2\text{H, m, CH}_2)$, $4.03(2\text{H, t, OCH}_2)$, $6.86(1\text{H, s, C3-H})$, $7.00(2\text{H, d, benzoate})$, $7.52\text{--}7.68(5\text{H, m, 2-phenyl})$, $7.95(2\text{H, ddX2, C7, 8-H})$, $8.05(1\text{H, d, C5-H})$, $8.17(2\text{H, d, benzoate})$. I.R.(KBr): $2900, 1730\text{ cm}^{-1}$. MS: $400(\text{M}^+)$. The samples were judged to be fully purified from TLC and DSC.

General syntheses of CABC: CABC series was prepared by the same procedure as that of Nakai *et al.* [2]. The mixture of 2,4-dihydroxybenzaldehyde (40 g, 0.29 mol), malononitrile (9.2 g, 0.29 mol) and piperidine (1 ml) were stirred at a temperature below 70°C for 1 h under nitrogen atmosphere. The precipitates obtained were washed with ethanol to give 2,4-dihydroxybenzylidene malononitrile(VI) as yellow needles in 53 per cent yield (26 g). The compound VI (26 g, 0.14 mol)/3.5 N HCl (1.8 l) solution was heated with stirring at 60°C for 1 h. The crude crystals obtained were recrystallized from ethanol, giving 3-cyano-7-hydroxycoumarin(VII) as yellow needles in 24 per cent yield; m.p. $> 300^\circ\text{C}$. Finally, CABC's were prepared by a conventional dehydrochloride reaction of compound VII and 4-*n*-alkoxybenzoyl chloride in the mixture of benzene and pyridine. The crude crystals were purified by several recrystallizations from toluene, giving 60–90 per cent yield as colourless needles. The crystals were identified as CABC, using I.R., N.M.R.: For example, CABC($n = 4$); $^1\text{H-N.M.R.}(\text{CDCl}_3)$: $\delta = 1.01(3\text{H, t, CH}_3)$, $1.53(2\text{H, m, CH}_2)$, $1.83(2\text{H, m, CH}_2)$, $4.06(2\text{H, t, OCH}_2)$, $7.00(2\text{H, d, benzoate})$, $7.33(2\text{H, m, C6,8-H})$, $7.67(1\text{H, d, C5-H})$, $8.13(2\text{H, d, benzoate})$, $8.28(1\text{H, s, C4-H})$. The samples obtained were judged to be fully purified by TLC and DSC.

2.2. Methods

Phase transitions were measured with a differential scanning calorimeter (Perkin Elmer DSC-1B) at a heating/cooling rate of 5 K min^{-1} . The texture of each mesophase was determined by a polarized microscope (Nikon, Optiphot-pol XTP-11) equipped with a Mettler FP-82 hot stage at a heating/cooling rate of 1 K min^{-1} under crossed polarizer. $^1\text{H-N.M.R.}$ spectra were recorded at 270 MHz (JEOL GX-270). I.R. spectra were measured with a JASCO A-302 spectrophotometer. Mass spectra were recorded on Hitachi RUM-6M.

3. Results and discussion

Figure 2 shows typical DSC curves for several samples. ABF compounds show nematic phase and CABC compounds exhibit smectic A phase. The nematic and smectic phases were identified from an appearance of nematic schliien texture and that of smectic A focal conic texture, respectively. In the $n = 5, 7$ samples of ABF, the melting point, T_m , undergoes a thermal hysteresis as seen in figure 2; the value of T_m at the second heating is lower than that at the first heating, but shifts to that at the first heating, as the sample is stored at room temperature after the first cooling process was run. This result indicates that metastable crystals are formed during the cooling process from the isotropic liquid state and gradually transform into stable crystals with storing at room temperature. The other ABF's showed usual melting behaviour. The melting behaviour of CABC is also complicated. As shown in figure 2, as a typical

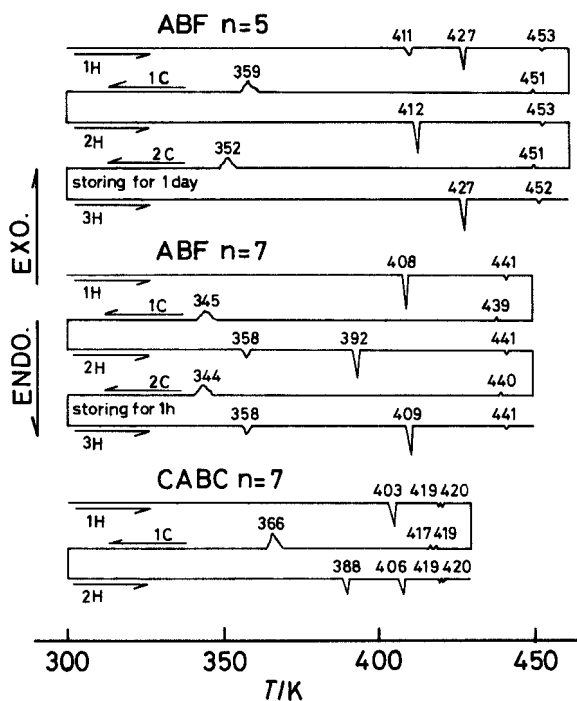


Figure 2. D.S.C. curves of three samples. nH : n th heating process, nC : n th cooling process.

example, the $n = 7$ crystals melt at 403 K to form smectic A state, which transforms into nematic state at 419 K and furthermore into isotropic liquid state at 420 K. At the second heating, one phase transition is seen at 388 K in the crystalline phase. In the $n = 9$, one phase transition appeared near 380 K in the crystalline state for all thermal processes and crystalline-smectic A phase transition occurred at 388 K. In the $n = 8$, the value of T_m at the first heating was 400 K but that at the second heating was 389 K, which indicates that metastable crystals are formed during the cooling process from the isotropic liquid state. The other CABCs showed usual melting behaviour.

Phase transition temperatures and the entropy changes for all the samples obtained from D.S.C. data are listed in the table. The data are shown only for the first heating. Figure 3 shows plots of phase transition temperature versus carbon number (n) of alkoxy group in alkoxybenzoyloxy substituents of ABF and CABC. ABF shows only nematic phase which has excellent thermal stabilities in a wide carbon number range of alkoxy group; even for $n = 1$, nematic phase is observed monotropically in the 1st cooling process, and smectic phase does not appear up to the long alkoxy group of $n = 12$. On the other hand, coumarin derivatives exhibit smectic A phase in the longer alkoxy groups than $n = 6$ but show no mesophase in the shorter alkoxy groups. Nakai *et al.* [2] pointed out that coumarin derivatives prefer to form smectic A phase, which was explained by the asymmetric and large dipole moment of coumarin skeleton; the dipole moment of about 4.9 D from the coumarin skeleton is preferably in perpendicular to the long molecular axis of CABC molecule. Dipole moments of flavone derivatives have not been measured but the polarity of flavone skeleton might be comparable to that of coumarin skeleton, because the dipole

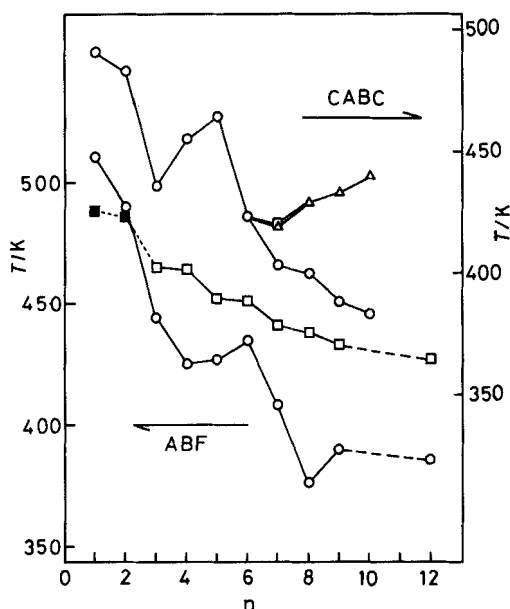


Figure 3. Phase transition temperatures versus carbon number of alkoxy group (n) for ABF and CABC. \circ , melting temperature, T_m , \square , nematic-isotropic liquid phase transition temperature, T_{N-I} ; \triangle , smectic A-isotropic liquid phase transition temperature, $T_{S_{A-I}}$; \blacksquare , monotropic isotropic liquid-nematic phase transition temperature, T_{I-N} .

moment of 2,6-dimethyl- γ -pyrone is reported to be 4.6 D [7]. Consequently, both positions of C=O and -O- in the skeleton and the substituents to the skeleton seem to sensitively affect the molecular packings in mesophase. On the other hand, by assuming that a molecule is in fully extended state and that twist angle between two planes of benzopyran 4-one ring and benzene ring in 6-benzoate/2-phenyl group, and that of coumarin skeleton and benzene ring in 7-benzoate group are 30° , CPK models were calculated for ABF ($n = 1$) and CABC ($n = 1$), using Cambridge Structural Database System [8]. So far as the extended conformation is assumed for a molecule, both ABF and CABC molecules are in linear-shaped on the CPK models, and the ratios of molecular length to molecular breadth (L/D) were estimated to be about 2.3 and 2.2 for ABF and CABC molecules, respectively. Therefore, the difference in the texture of mesophase between ABF and CABC may be not explained by either the molecular shape and the size from the CPK models. Generally, the molecular packings in the mesophase may reflect the molecular arrangements of the crystals. The structures of crystals of coumarin and flavone derivatives have been determined by several researchers [9], using X-ray diffraction method; the structures in the crystals remarkably change by the substituents and their positions to the skeleton. We are progressing X-ray diffraction work on the ABF and CABC crystals. The crystals of ABF ($n = 3$) are triclinic, space group P1 with cell dimensions $a = 13.918 \text{ \AA}$, $b = 16.306 \text{ \AA}$, $c = 13.918 \text{ \AA}$, $\alpha = 99.795^\circ$, $\beta = 107.235^\circ$, $\gamma = 72.328^\circ$, $Z = 6$. The detailed structure of the crystals will be published elsewhere with the structures of CABC crystals after the structure determination is more refined [10]. In the ABF ($n = 3$) crystals, however, the planes of flavone skeleton in two adjacent ABF molecules are almost perpendicular to each other, and the ABF molecules are packed almost in head-to-tail structure. Inferring from the above results, the lateral

Phase transition temperatures and the entropy changes of ABF and CABC.

Sample	<i>n</i>	T_m/K	$T_{S_A-N}/T_{S_A-I}/\text{K}$	T_{N-I}/K
		$\Delta S_m/\text{JK}^{-1}\text{mol}^{-1}$	$\Delta S_{S_A-N}/\Delta S_{S_A-I}/\text{JK}^{-1}\text{mol}^{-1}$	$\Delta S_{N-I}/\text{JK}^{-1}\text{mol}^{-1}$
ABF	1	510		(488)
		$\frac{97}{}$		
	2	490		(486)
		$\frac{97}{}$		
	3	444		$\frac{465}{2}$
		$\frac{68}{}$		
	4	425		$\frac{464}{2}$
		$\frac{75}{}$		
	5	427		$\frac{452}{2}$
		$\frac{75}{}$		
	6	435		$\frac{451}{2}$
		$\frac{88}{}$		
7	408		$\frac{441}{2}$	
	$\frac{81}{}$			
8	376		$\frac{437}{2}$	
	$\frac{92}{}$			
9	390		$\frac{433}{2}$	
	$\frac{97}{}$			
12	386		$\frac{427}{2}$	
	$\frac{121}{}$			
CABC	1	491		
		$\frac{88}{}$		
	2	483		
		$\frac{89}{}$		
	3	436		
		$\frac{92}{}$		
	4	455		
		$\frac{93}{}$		
	5	464		
		$\frac{108}{}$		
6	426			
	$\frac{87}{}$			
7	403	$\frac{419}{3}$	$\frac{420}{3}$	
	$\frac{100}{}$			
8	400	$\frac{429}{4}$		
	$\frac{116}{}$			
9	388	$\frac{433}{5}$		
	$\frac{76}{}$			
10	383	$\frac{440}{7}$		
	$\frac{101}{}$			

T_m and ΔS_m : melting temperature and the entropy change. T_{S_A-N} and ΔS_{S_A-N} : smectic A-nematic phase transition temperature and the entropy change. T_{S_A-I} and ΔS_{S_A-I} : smectic A-isotropic liquid phase transition temperature and the entropy change. T_{N-I} and ΔS_{N-I} : nematic-isotropic liquid phase transition temperature and the entropy change.

intermolecular interaction seems to be weak in ABF ($n = 3$) crystals, and this may explain why the ABF's show the nematic phase, although further X-ray diffraction work is necessary for an explicit answer.

In conclusion, the present work indicates that flavone derivatives tend to form nematic phase in contrast with coumarin derivatives which have smectic A phase.

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