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Thermal and Dielectric Properties of Liquid Crystals with a Coumarin Skeleton

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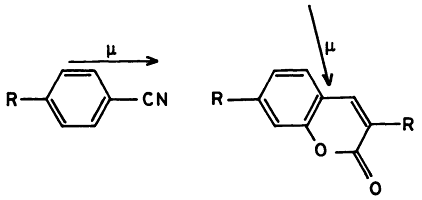
In order to examine the liquid crystalline properties of coumain, 3-X- and 7-Y-substituted coumarins where X= cyano and *n*-alkoxycarbonyl, and Y=4-*n*-alkyl- and 4-*n*-alkoxybenzoyl, 4-alkoxycinnamoyloxy, 4′-alkyl- and 4′-alkoxy-4-biphenylylcarbonyloxy, and 4-(4-alkoxybenzoyloxy)benzoyloxy (**4**) groups have been prepared. The compounds with X=alkoxycarbonyl group tend to exhibit strong smectic properties, and compounds with X=cyano exhibit stable nematic phases, whereas the coumarin core seems to facilitate a lateral separation of molecules in the mesophase due to its large molecular breadth. The heptyloxy homolog of **4** exhibits a reentrant behavior of the C–N_{re}–S_A–N–I type. The thermal properties are discussed in terms of the polarity and polarizability of coumarin, and the molecular structure. The dielectric properties of the compounds have also been examined and discussed in terms of the polarity of the coumarin core.

An investigation of the physical properties of new liquid crystalline materials is important in studying the relationship between the structure of materials and their mesomorphic characteristics. Liquid crystalline materials with a polar group such as a cyano or a nitro give rise to some interesting behavior. A cyano group directed along the parallel direction with respect to the longer molecular axis induces a strong dipole moment along that direction. Liquid crystals with a cyano group as the terminal of the molecule have proved successful in electro optical devices employing the twisted nematic mode. On the other hand, a cyano group directed along the lateral direction with respect to the longer molecular axis induces a strong dipole moment along that lateral direction. Liquid crystals with a cyano group as a lateral substituent give rise to a negative dielectric anisotropy and have proved successful in electro-optical devices employing the dynamic scattering and guest-host modes.[1]



In usual mesogens, the polarity is important in determining not only the mesomorphic but also the dielectric properties. Benzonitrile has a strong dipole moment (3.9 D, 1 D=3.3356×10^{-30} C m) along the longer molecular axis, as is shown below.[2] On the other hand, coumarin is a benzene derivative with a lactone ring, which generates a strong dipole monent (4.48 D).[3] As the 3 and 7 positions of coumarin are substituted, however, the polarity will have some angles with respect to the longer molecular axis. In this paper, we wish to report the syntheses of new liquid crystalline materials involving coumarin; their thermal and dielectric properties will be discussed in terms of the characteristics of the coumarin core.

Experimental

Method. The transition temperatures were determined using a Nikon Model POH polarising microscope fitted with a Mettler FP 52 heating stage and a FP 5 control unit. The transition entropies were calculated by means of the equation; $\Delta S=\Delta H/T$, where the transition enthalpy, ΔH, was measured with a Daini-Seikosha SSC-560 differential scanning calorimeter, indium being used as a calibration standard, with a heating rate of 5 °C/min. The dielectric constants were measured by using a Ando-denki TR-10 precision capacitance-measurement system. The capacitor cell consisted of two indium oxide-coated glass electrodes separated by a 25 μ Mylar spacer. The cell temperature was controlled by means of a brass housing. The voltage applied was 0.4 V at 1 kHz. The alignment of molecules in the cell was achieved by applying a magnetic field of *ca.* 8 kG (1 G=10^{-4} T). The capacitor cell was calibrated by the use of highly purified benzene and acetonitrile.

Materials. Nematic 5 and ZLI-1083 were purchased from the Merck Co. The 4-(*n*-alkyl)benzoic acids and the aldehydes were purchased from the Kantokagaku Co. The 4-(*n*-alkoxy)benzoic acids and the aldehydes were purchased from the Tokyo Kasei Co.

3-Cyano-7-hydroxycoumarin. A mixture of 2,4-dihydroxybenzaldehyde (5 g, 0.036 mol) and malonitrile (2.4 g, 0.036 mol) in absolute ethanol (30 ml) and two drops of piperidine was heated with stirring at 70 °C for 1 h. The reaction mixture was then poured onto a 350-ml portion of 3.5 mol dm^{-3} hydrochloric acid, and the resulting solution was heated at 60 °C for 30 min. After cooling, the precipitates were collected by filtration and recrystallized from ethanol, giving 3-cyano-7-hydroxycoumarin as yellow needles, 3.6 g (53%); mp>270 °C.[4]

3-Pentyloxycarbonyl-7-hydroxycoumarin. A mixture of 2,4-dihydroxybenzaldehyde (11 g, 0.08 mol), dipentyl malonate (20.1 g, 0.082 mol), piperidine (0.8 ml), and three drops of acetic acid in absolute ethanol (25 ml) was refluxed for 5 h.[5] The reaction mixture was then poured onto hot water (50 ml) and left to stand for overnight. The precipitates that separated out were collected and recrystallized from methanol, giving 3-pentyloxycarbonyl-7-hydroxycoumarin as colorless needles, 6.0 g (27%).

The 3-alkyloxycarbonyl-7-hydroxycoumarins were prepared by a similar method.

The 4-alkyl- and 4-alkoxybenzoyl chlorides and the coumarins were reacted in a mixture of absolute pyridine and benzene (1 : 1) to give a homologous series of **1**.[6]

The 4-alkoxycinnamic acid chlorides, which had been obtained by the reaction of 4-alkoxybenzaldehydes and malonitrile, and the coumarins were reacted in a mixture of

TABLE 1. ELEMENTARY ANALYSIS DATA

Compound	Formula	Calcd (%)			Found (%)		
		C	H	N	C	H	N
1a	$C_{27}H_{30}O_7$	69.51	6.48		69.26	6.51	
1b	$C_{26}H_{28}O_6$	71.54	6.47		71.48	6.46	
1c	$C_{27}H_{30}O_7$	69.51	6.48		69.32	6.38	
1d	$C_{28}H_{32}O_7$	69.98	6.71		69.95	6.67	
1e	$C_{29}H_{34}O_7$	70.43	6.93		70.45	7.01	
1f	$C_{30}H_{36}O_7$	70.85	7.13		70.69	7.04	
1g	$C_{27}H_{30}O_7$	69.51	6.48		69.38	6.35	
1h	$C_{28}H_{32}O_7$	69.98	6.71		69.73	6.64	
1i	$C_{22}H_{19}NO_4$	73.11	5.30	3.88	72.85	5.26	3.94
1j	$C_{25}H_{25}NO_4$	74.42	6.25	3.47	74.22	6.26	3.40
1k	$C_{23}H_{21}NO_5$	70.57	5.41	3.58	70.39	5.25	3.49
1l	$C_{24}H_{23}NO_5$	71.10	5.72	3.45	71.10	5.78	3.53
1m	$C_{25}H_{25}NO_5$	71.58	6.01	3.34	71.45	6.00	3.36
1n	$C_{23}H_{19}NO_6$	68.15	4.72	3.45	67.89	4.67	3.39
1o	$C_{24}H_{21}NO_6$	68.72	5.05	3.34	68.50	5.03	3.23
2a	$C_{25}H_{24}O_7$	68.80	5.54		68.78	5.55	
2b	$C_{27}H_{28}O_7$	69.81	6.08		69.93	6.18	
2c	$C_{27}H_{28}O_7$	69.81	6.08		69.65	6.16	
2d	$C_{29}H_{32}O_7$	70.71	6.55		70.65	6.57	
2e	$C_{23}H_{19}NO_5$	70.94	4.92	3.60	70.76	4.77	3.51
2f	$C_{25}H_{23}NO_5$	71.93	5.55	3.36	71.94	5.56	3.35
2g	$C_{28}H_{32}O_7$	69.98	6.71		69.80	6.69	
3a	$C_{27}H_{22}O_6$	73.29	5.01		73.25	5.02	
3b	$C_{28}H_{24}O_6$	73.67	5.30		73.69	5.37	
3c	$C_{29}H_{26}O_6$	74.03	5.57		73.96	5.59	
3d	$C_{30}H_{28}O_6$	74.37	5.82		74.35	5.83	
3e	$C_{31}H_{30}O_6$	74.69	6.06		74.72	6.01	
3f	$C_{32}H_{32}O_6$	74.98	6.29		74.91	6.28	
3g	$C_{29}H_{26}O_7$	71.59	5.39		71.42	5.33	
3h	$C_{31}H_{30}O_7$	72.36	5.88		72.42	5.91	
3i	$C_{26}H_{19}NO_4$	76.27	4.68	3.42	76.27	4.61	3.42
3j	$C_{27}H_{21}NO_5$	73.79	4.82	3.19	73.80	4.78	3.16
4a	$C_{26}H_{17}NO_7$	68.57	3.76	3.08	68.56	3.64	2.99
4b	$C_{27}H_{19}NO_7$	69.08	4.08	2.98	69.33	4.17	3.07
4c	$C_{28}H_{21}NO_7$	69.56	4.38	2.90	69.57	4.19	2.85
4d	$C_{29}H_{23}NO_7$	70.01	4.66	2.82	70.02	4.61	3.05
4e	$C_{30}H_{25}NO_7$	70.44	4.93	2.74	70.65	4.97	2.65
4f	$C_{31}H_{27}NO_7$	70.84	5.18	2.67	70.74	5.08	2.51
4g	$C_{32}H_{29}NO_7$	71.22	5.42	2.60	71.29	5.39	2.42
4h	$C_{33}H_{31}NO_7$	71.60	5.64	2.53	71.47	5.61	2.78

absolute pyridine and benzene (1 : 1) to give a homologous series of **2**.

The 4-alkyl- and 4-alkoxy-4′-carboxybiphenyls were prepared by the method of Gray *et al.*[7] Series **3** were obtained by the condensation of 4-alkyl- and 4-alkoxy-4′-(chlorocarboyl)biphenyls and coumarins in a mixture of absolute pyridine and benzene (1 : 1).

The 4-(4-alkoxybenzyloxy)benzoic acids were obtained according to the method of van Meter *et al.*[8] Series **4** were obtained by the condensation of the 4-(4-alkoxybenzoyloxy)-benzoyl chlorides and 3-cyano-7-hydroxycoumarin in a mixture of absolute pyridine and benzene (1 : 1). 4-Pentylphenyl 4-(4-octylbenzoyloxy)benzoate was prepared by the method of Dubois *et al.*[9]

N-[4-[4-(Octyloxy)benzoyloxy]benzylidene]-4-cyanoaniline was prepared by the method of Demus *et al.*[10] The products were purified by column chromatography on silica gel, using a mixture of pet. ether and ether (95 : 5—90 : 10) as an elution solvent, followed by recrystallization from absolute ethanol.

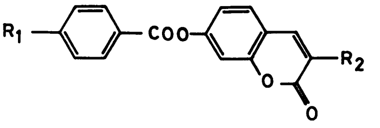
The purity was checked by means of the elementary analysis; the results are shown in Table 1.

Results

The transition temperatures and entropies for Series **1**—**4** are summarized in Table 2—5. The virtual N–I transition temperature for **1c**, **1f**, and **1m** were evaluated[11] from the binary phase diagrams in Fig. 1. The nematic and smectic phases for the compounds with an alkoxycarbonyl group tend to exhibit a schlieren texture and fan shaped texture, respectively, between two glass plates.

The compounds with a cyano group tend to form the nematic and/or smectic phases with a homeotropic texture between two glass plates. To identify the

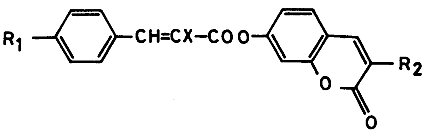
Table 2. Transition temperatures (°C) for series **1**



	R_1	R_2	C	S_A	N	I
1a	$C_8H_{17}O$	$COOC_2H_5$	. 129.7	— (106.1)	— (107.5)	.
1b	C_5H_{11}	$COOC_4H_9$	. 120.5		—	.
1c	$C_6H_{13}O$	$COOC_4H_9$	. 84.1	— 96.4	— [89]	.
1d	$C_7H_{15}O$	$COOC_4H_9$	. 80.4	. 101.1	—	.
1e	$C_8H_{17}O$	$COOC_4H_9$	. 82.2	. 105.4	—	.
1f	$C_8H_{17}O$	$COOC_5H_{11}$	. 74.7	. 108.5	— [92]	.
1g	C_4H_9O	$COOC_6H_{13}$	. 92.3	— (87.1)	—	.
1h	$C_6H_{13}O$	$COOC_5H_{11}$	. 93.0	— (92.1)	—	.
1i	C_5H_{11}	CN	. 127.9	—	— (110.0)	.
1j	C_8H_{17}	CN	. 125.4	. 131.6	—	.
1k	$C_6H_{13}O$	CN	. 154.2	—	. (144.9)	.
1l	$C_7H_{15}O$	CN	. 133.4	. 148.9	. 150.1	.
1m	$C_8H_{17}O$	CN	. 129.0	. 157.9	. [152]	.
1n	CN	$COOC_5H_{11}$	. 138.7	—	—	.
1o	CN	$COOC_6H_{13}$	. 137.3	—	—	.

The values in parentheses and brackets indicate the monotropic and virtual transition temperatures respectively. The presentation of this table is refered to Ref. 15.

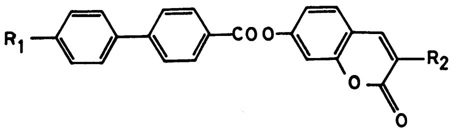
Table 3. Transition temperatures (°C) for series **2**



	R_1	R_2	X	C	S_A	N	I
2a	C_4H_9O	$COOC_2H_5$	H	. 151.7	—	.	.
2b	$C_6H_{13}O$	$COOC_2H_5$	H	. 139.4	. 142.8	. 157.7	.
2c	C_4H_9O	$COOC_4H_9$	H	. 97.5	. 129.0	—	.
2d	C_4H_9O	$COOC_6H_{13}$	H	. 104.1	. 132.1	—	.
2e	C_4H_9O	CN	H	. 157.6	—	. 213.1	.
2f	$C_6H_{13}O$	CN	H	. 133.0	. 186.5	. 203.8	.
2g	C_4H_9O	$COOC_4H_9$	CH_3	. 98.4	—	—	.

smectic phase, the binary-phase diagrams for several compounds were examined, as is shown in Figs. 1 and 2. Figure 1a indicates a phase diagrams for the binary mixture of 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate and **1c**, where both smectic A phases are miscible. This indicates that the smectic phase for **1c** can be assigned to the smectic A modification.[9] **4f** shows a reentrant property of the C–N_{re}–S_A–N–I type, which is confirmed by the binary-phase diagrams shown in Figs. 2c and 2d. The latent heats of the N_{re}–S_A and S_A–N transitions for **4f**—**h** are so small that these transitions could not be detected by means of the DSC thermograms. On the basis of these facts, we assume that the enthalpies for these transitions are less than 50 J mol^{-1}. The extrapolation of the N–I transition temperatures in Fig. 2c gives the N–I transition temperature of 295 °C for **4f**. Similarly, the N–I transition temperatures for **4g** and **4h** were evaluated as *ca.* 300 °C.

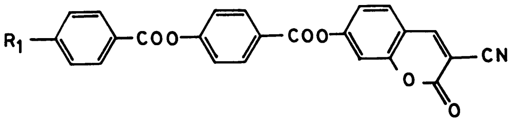
Table 4. Transition temperatures (°C) and entropies (J K^{-1} mol^{-1}) for series **3**



	R_1	R_2	C	S_A	N	I	ΔS_{N-I}
3a	C_3H_7	$COOCH_3$	. 179.6	. (160.2)	. [278]	.	—
3b	C_3H_7	$COOC_2H_5$	. 166.0	. 194.2	. 249.7	.	0.8
3c	C_3H_7	$COOC_3H_7$	. 142.3	. 207.3	. 236.6	.	1.4
3d	C_3H_7	$COOC_4H_9$	. 126.3	. 207.2	. 216.4	.	1.0
3e	C_3H_7	$COOC_5H_{11}$	. 136.4	. 207.3	. 214.4	.	1.0
3f	C_3H_7	$COOC_6H_{13}$	. 127.3	. 207.6	—	.	
3g	C_2H_5O	$COOC_4H_9$	. 140.9	. 228.0	. 261.8	.	0.9
3h	C_4H_9O	$COOC_4H_9$	. 138.5	. 241.5	—	.	
3i	C_3H_7	CN	. 210.0	—	. >300	.	
3j	C_4H_9O	CN	. 180.2	—	. >300	.	

The values in parenthesis and bracket are the monotropic transition temperatures.

Table 5. Transition temperatures (°C) for series **4**



	R_1	C	N_{re}	S_A	N	I
4a	C_2H_5O	. 210.8	—	—	. >300	.
4b	C_3H_7O	. 209.8	—	—	. >300	.
4c	C_4H_9O	. 189.8	—	—	. >300	.
4d	$C_5H_{11}O$	. 162.8	—	—	. >300	.
4e	$C_6H_{13}O$	. 154.1	—	—	. >300	.
4f	$C_7H_{15}O$	. 145.9	. 147.6	. 227.4	. [295]	.
4g	$C_8H_{15}O$	. 146.6	.	. 247.1	. [300]	.
4h	$C_9H_{19}O$	. 150.3	—	. 255.1	. [300]	.

The values in the brackets are the virtual transition temperatures.

The dielectric constants were measured in a eutectic mixture of azoxy compounds (Merck nematic 5), since the present homologues have relatively high melting points. Figure 3 indicates the plots of the dielectric constants $\varepsilon_{//}$, $\varepsilon_{\perp}$, and $\Delta\varepsilon$ against the mole concentration of the coumarin compounds, where $\varepsilon_{//}$, $\varepsilon_{\perp}$, and $\Delta\varepsilon$ are the dielectric constants along the parallel and perpendicular directions with respect to the longer molecular axis, and the difference, respectively. In Fig. 3a, both $\varepsilon_{//}$ and $\varepsilon_{\perp}$ for **1c** can be seen to increase linearly in the range between 0 and 30 mol%, and to reach a plateau onward. The anisotropy also increases similarly in the range between 0 and 30 mol% of **1c** and then decrease monotonically thereafter, giving a maximum at 25 mol% of **1c**. **2c** also shows a similar trend. In Fig. 3b, both $\varepsilon_{//}$ and $\varepsilon_{\perp}$ for **1i** increase linearly with an increase in the concentration of **1i** in the range between 0 and 30 mol% of **1i**, though they tend to reach a plateau thereafter. A similar trend is also observed in **2f** and **4d**. Thus, the plots of the dielectric anisotropies against the mole

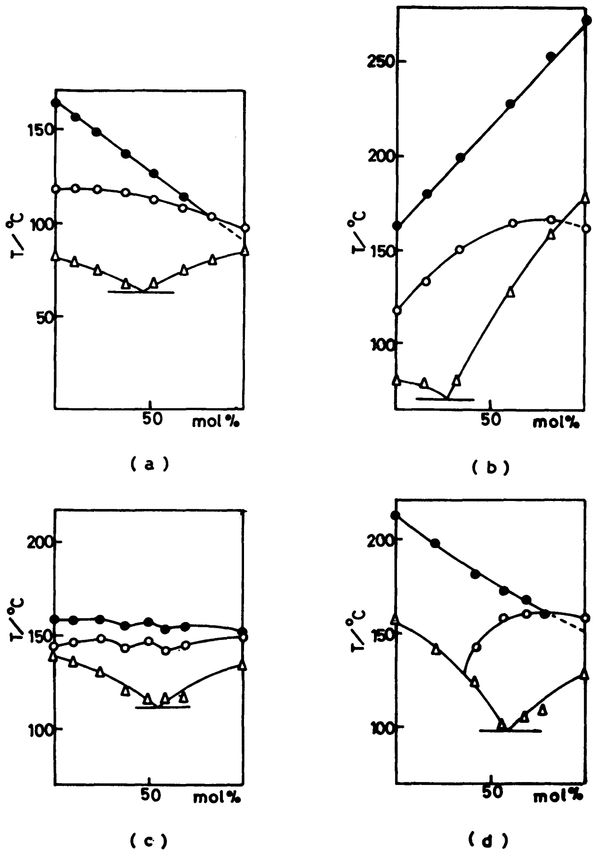


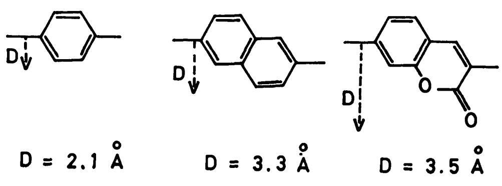
Fig. 1. Phase diagrams for the mixtures of (a) 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate (on left) and **1c** (on right), (b) 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate (on left) and **3a** (on right), (c) **2b** (on left) and **1l** (on right), (d) **2f** (on left) and **1m** (on right).
●; Nematic-isotropic, ○; smectic A-nematic, and △; crystal-smectic A (nematic) transitions.

concentration for the present series have no linear correlation. The dielectric anisotropies at 15 mol% of the compounds are illustrated in Table 5.

Discussion

It has been known that the linearity, rigidity, and polarizability of a molecule are very important in determining the stability of the mesophase. From the structural point of view, the present series might be unfavorable for the stability of the nematic phase, since coumarin has a larger molecular breadth than phenyl and naphthyl groups, as is shown below.[12] Although coumarin elongates the molecular length of 1.5 Å compared with benzene, simultaneously the breadth around coumarin is larger by 1.7 times than that of benzene.

The thermal stability of the mesophase for the present series is compared with those of the other related series



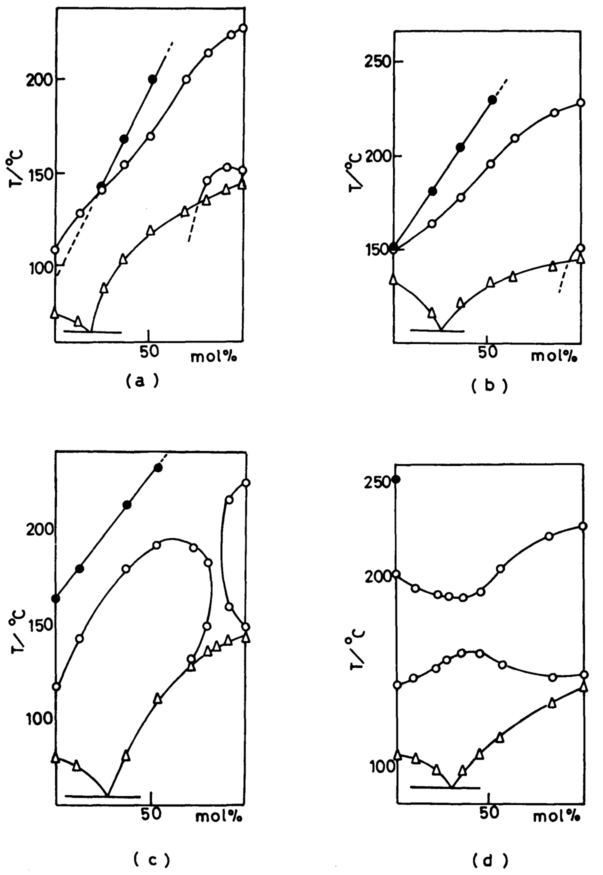


Fig. 2. Phase diagrams for the mixtures of (a) **1f** (on left) and **4f** (on right), (b) **1l** (on left) and **4f** (on right), (c) 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate (on left) and **4f** (on right), (d) *N*-[4-[4-(octyloxy)benzoyloxy]benzylidene]-4-cyanoaniline (on left) and **4f** (on right).
●; Nematic-isotropic, ○; smetic A-nematic, and △; crystal-smectic A (nematic) transitions.

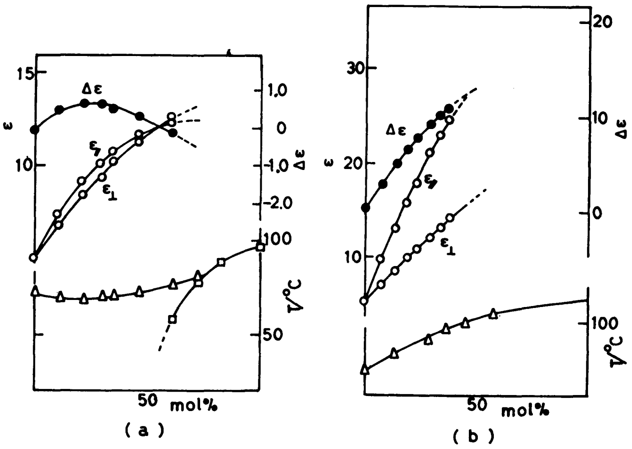


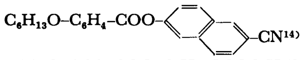
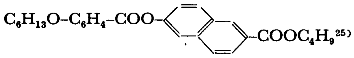
Fig. 3. Plots of dielectric constants ($\varepsilon_{//}$ and $\varepsilon_{\perp}$) and dielectric anisotropy ($\Delta\varepsilon$) and nematic-isotropic and smectic A-nematic (isotropic) transition temperatures against concentration (mol%) for the binary mixtures of (a) nematic 5 (on left) and **1c** (on right), (b) nematic 5 (on left) and **1i** (on right).
△; Nematic-isotropic and □; smectic A-nematic (isotropic) transitions.

Table 6. Dielectric constants $\varepsilon_{//}, \varepsilon_{\perp}$, and $\Delta\varepsilon$

Compound	15 mol%		
	$\varepsilon_{//}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$
1c	8.0	7.5	0.5
2c	8.0	7.3	0.7
1i	13.6	8.6	5.0
2f	12.9	7.7	5 2
4d	14 2	7.2	7.0
10	5.9	5.4	0.5
ZLI-1083	8.5	5.7	2.8
Nematic 5 (neat)	5.0	5.1	−0.1

All data were taken in Nematic 5 at 60±1 °C.

below, where the transition temperatures for the compounds selected for the comparative study are shown:

		C		S$_A$		N		I
5	$C_6H_{13}O–C_6H_4–COO–C_6H_4–CN$[13]	.	70.5	—		.	81.0	.
6	$C_6H_{13}–C_6H_4–COO–C_6H_4–CH=CH–CN$[13]	.	97.5	—		.	147.7	.
7	$C_6H_{13}O–C_6H_4–CH=CH–COO–C_6H_4–CN$[13]	.	73.4	—		.	134.3	.
8	 $C_6H_{13}O–C_6H_4–COO–$ –CN[14]	.	95	—		.	160	.
9	$C_6H_{13}O–C_6H_4–COO–C_6H_4–OCOC_4H_9$[15]	.	68	—		.	93	.
10	 $C_6H_{13}O–C_6H_4–COO–$ –$COOC_4H_9$[25]	.	94.7	.	107.2	.	107.6	.

($–C_6H_4–$ indicates a *p* phenylene group.)

Coumarin compounds **1a**—**f** with a alkoxycarbonyl group at the 3 position exhibit strong smectic properties in addition to the nematic ones. The thermal stability of the nematic phase is comparable with those for **9** and **10**. Similar trends are observed in Series **2** and **3**. For the homologous series, somewhat interesting trends are observed in the effect of chain length on the thermal stabilities of the nematic and smectic A phases. The S$_A$–N transition temperatures for **1c**—**e** and **3g**—**h** increase with an increase in the carbon number in the alkyl chain at the 7 position (see Tables 2 and 4). These trends are always present. By contrast, the S$_A$–N transition temperatures for **1a**, **1e**, **1f**, and **3b**—**f**, which involve the alkyl chain of the ethyl to the hexyl group at the 3 position of the coumarin core almost constant (see Tables 2 and 4). Simultaneously, the N–I transition temperatures rapidly decrease, showing a weak even-odd alternation. In this connection, the following facts are worthy of note. Firstly, it would be reasonable to assume that the coumarin facilitates the formation of the smectic order, since the strong dipole moment arising from the coumarin core is directed to the lateral direction of the molecule, and that it increases the lateral interactions. Secondly, the alkoxycarbonyl group at the 3 position of coumarin should be located on the coumarin plane due to steric hindrance between the alkoxycarbonyl and carbonyl groups at the 2 position of coumarin, thus increasing the molecular thickness. Therefore, the elongation of the alkyl chain in the alkoxycarbonyl group would facilitate the lateral separation of the molecules in the mesophase, rapidly decreasing the thermal stability of the nematic phase. Thereby, the increase in the alkyl chain length would not serve to enhance the S$_A$–N transition temperatures, since the lateral separation of the molecules inhibits any short-range interaction, a general requisite for the enhancement of the smectic properties.

When a cyano group is introduced at the 3 position, both S$_A$–N and N–I transition temperatures tend to decline for Series **1**—**4**, and the nematic properties become remarkable. For example, the N–I transition temperature for **1k** is higher than **5** by 64 °C and lower than **8** by only 15 °C, while the N–I temperature for **1i** is lower than **6** by 38 °C. On the other hand, the homologous series of **4** form a highly stable nematic phase. These facts indicate that the polarity and polarizability arising from the coumarin core involving the cyano group and the elongation of the rigid core of the molecule along the longer axis enhance the stability of the nematic phase, though the large molecular breadth around the coumarin core does not favor the nematic stability. An interesting trend is observed in the thermal properties for **1n** and **1o**. These do not exhibit a nematic phase, but these compounds have a cyano group at the terminal. These facts indicate that the alkoxycarbonyl group at the 3 position of coumarin decreases the N–I transition temperature as a result of the increased molecular thickness, as has been mentioned above. The homologous series of **4** have a highly stable nematic phase.

The smectic A phase commences from the heptyloxy homologue, and the heptyloxy homologue shows a reentrant behavior of the C–N$_{re}$–S$_A$–N–I type. As has been demonstrated by several authors,[16,17] the formation of a bimolecular complex is indispensable for the reentrant phenomena. It has been known that molecules exhibiting the reentrant behavior are constituted of plural phenyl rings combined by linkages such as –CH=N– or –COO–, with an alkoxy group of a suitable length as a terminal and a polar group such as a cyano or a nitro group indispensable to form a bimolecular complex.[18,19] In Fig. 1a, the S$_A$–N transition temperatures show an almost straight line, and both S$_A$ phases are miscible, indicating that **1c** forms the smectic A phase with a monolayer organization of the molecules, because 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate has been known to form the smectic A phase.[25]

Both smectic A phases in Fig. 1b show a miscible relation with a convexity, indicating that the smectic A phase for **3a** also has a monolayer alignment of molecules. Therefore, it is impossible to expect the homologous series of **3** to exhibit the reentrant behavior. In fact, the homologous series do not exhibit the reentrant behavior, whereas they do show a wide range of the smectic A phase (Table 4).

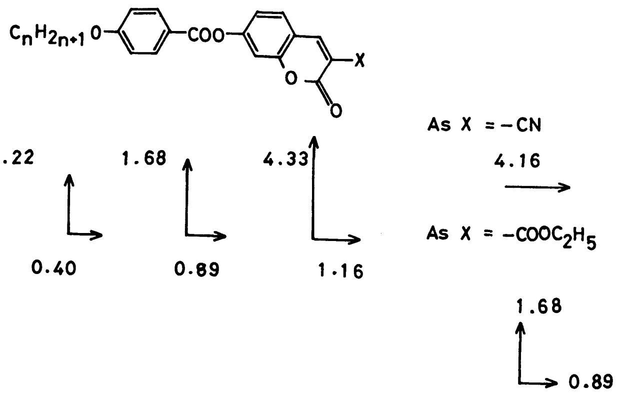
In Fig. 1c, the smectic A phase for **2b** is miscible with that for **1n**, whereas the smectic A phase for **1n** is considered to form a bilayer type of alignment of the molecules, since the molecule has the cyano group as the polar terminal.[18,19] In Fig. 1d, on the other hand, the S$_A$–N transition temperatures show a remarkable depression between 40 and 60 mol% of **2o**, whereas both **1o** and **2f** have the cyano group as the terminal.

In Figs. 2a and 2b, the smectic A phases for **1f** and **1n** are miscible with that for **4f**. An interesting fact is that the reentrant N$_{re}$–S$_A$ transition temperatures for **4f** increases with an increase in the concentration of **1f** but rapidly decrease thereafter, giving a maximum at 11 mol% of **4f** (Fig. 2a), whereas these temperatures rapidly decrease with an increase in the concentration of **11** (Fig. 2b). A tentative description of this trend is shown in Fig. 2c, where the monolayer smectic A phase for 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate is immiscible with the bilayer smectic A phase for **4f**. These facts indicate very clearly that a very subtle change in the molecular structure determines the affinity between the monolayer and bilayer-type smectic A phases. As we can see from Fig. 2d, the bilayer smectic A phase shows a remarkably constricted part at 60 mol% of **4f**, presumably as a result of the subtle difference in their molecular structures. Indeed, the smectic A phase with the monolayer alignment of molecules has been known usually to have an affinity with the bilayer one, but sometimes not.[20,21]

According to a concept of the miscibility relation between the monolayer and bilayer smectic A phases in the pure molecule, we can easily understand the reentrant phenomena.

The molecules with a polar terminal group such as cyano have been known to form the bimolecular complex in the mesophase and in an isotropic solution as a result of strong dipole-dipole interactions.[22,23] Such interactions form the bilayer alignment of the molecules in the smectic A phase. Usually, the bilayer smectic A phase is more stable than the monolayer one at higher temperatures. Therefore, the bilayer smectic A organization would vary in relation to the monolayer one with a lowering of the temperature. As the bilayer smectic A phase does not, thereby have a miscible relation with the monolayer one, we can expect the molecule to exhibit the reentrant phenomena. **4f** is just such a case. Further study is now underway.

Dielectric Propererties. It has been known that polarity is very important in determining the dielectric properties of a molecule. Therefore, we have to pay much attention to the polarity of coumarin. As has been mentioned above, coumarin has a larger dipole moment than benzonitrile, though the dipole moment in the present series is directed to the lateral direction of the molecule. We can roughly estimate the effective dipole moment, by the use of the usual method.[2,24]



Supposing the order parameter in the nematic phase to be 0.6, we can expect the molecule with X=H to show a negative dielectric anisotropy, since $\mu=-0.46$. The alkoxycarbonyl compounds can be expected to show small positive dielectric anisotropies, for the effective dipole moment is estimated to be $+0.007$. As the cyano group is introduced at the 3 position of coumarin, the effective dipole moment is estimated to have a value of 2.91, as the 3-cyano compounds can be expected large dielectric anisotropies. As the phenyl group in **1a**—**h** is replaced by a cyclohexane, we can expect to exhibit large negative dielectric anisotropies. Unfortunately, 3-alkoxycarbonyloxy-7-(4-alkylcyclohexylcarbonyloxy)-coumarins exhibited only smectic properties.[25]

In Fig. 3a, the plots of the dielectric constants *versus* the mole concentration show rather interesting trends. The anisotropy increases with an increase in the concentration of **1c** and decreases monotonically, giving a maximum at 25 mol%. The extrapolated value for **1c**, therefore, is -1.5, incline the calulated result. In this case, we assume that the monotonical decrease in the range between 25 and 100 mol% of **1c** is connected with the increases in the smectic order in the mixture, as shown is in Fig. 3a, and that **1c** has essentially a positive dielectric anisotropy. In Fig. 3b, the dielectric anisotropy for **1i** linearly increases with increasing the concentration of **1i** and tends to become a plateau, the curve having an forward convexity. Therefore, **1i** must have a large positive dielectric anisotropy.

As we can see by comparing the dielectric constants of butyl 6-[4-(hexyloxy)benzoyloxy]-2-naphthoate (**1c** and **2c**) in Table 5, the dipolarity arising from the coumarin core results in an increase to the same extent in the dielectric constants along both parallel and perpendicular directions of the molecule. As a result, the dielectric anisotropies for **1c** and **2c** are almost same as that for the naphthalene compound. As the alkoxycarbonyl group at the 3 position is replaced by the cyano, the dielectric constant along the parallel direction of the molecule tends to increase rapidly, though that along the perpendicular direction stays constant, resulting in large values of the dielectric anisotropy.

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