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The Preparation and Thermal Properties of Terminal Disubstituted *N*-(4-Benzoyloxybenzylidene)anilines

Shunsuke Takenaka,* Tetsuya Ikemoto, and Shigekazu Kusabayashi
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565
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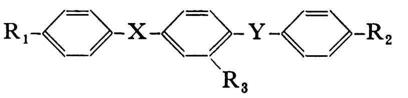
Synopsis. The homologous series of *N*-[4-(4-*n*-alkoxybenzoyloxy)benzylidene]-4-(2-methylbutoxy)aniline (**1**), and *N*-[4-[4-(2-methylbutoxy)benzoyloxy]benzylidene]-4-*n*-alkoxyaniline (**2**), and *N*-[4-(4-*n*-alkoxybenzoyloxy)-3-hydroxybenzylidene]-4-(2-methylbutoxy)aniline (**3**) where the 2-methylbutoxyl group has an S-configuration, have been prepared. Series **1** and **2** form a chiral smectic C (S_C^*) phase in addition to a cholesteric (Ch) and a chiral smetic G (S_G^*) phases, and series **3** form (S_C^*) and Ch phases.

It has been known that three-ring compounds incorporating ester **4** or azomethine **5** linkages display highly stable liquid crystalline phases.[1,2)]



1 X = -COO-, Y = -CH=N-, $R_1 = n\text{-}C_nH_{2n+1}O\text{-}$, R_2 = 2MBO-, R_3 = H-

2 X = -COO-, Y = -CH=N-, R^1 = 2MBO-, $R_2 = n\text{-}C_nH_{2n+1}O\text{-}$, R_3 = H-

3 X = -COO-, Y = -CH=N-, $R_1 = n\text{-}C_nH_{2n+1}O\text{-}$, R_2 = 2MBO-, R_3 = HO-

4 X = -COO-, Y = -OOC-, R_1, $R_2 = n\text{-}C_nH_{2n+1}O\text{-}$, R_3 = H-

5 X = -N=CH-, Y = -CH=N-, R_1, $R_2 = n\text{-}C_nH_{2n+1}O\text{-}$, R_3 = H-

(2MBO- = (*S*)-2-methylbutoxy)

Series **4** in which the linkages are relatively polar, and flexible, display stable nematic (N), smectic A and C phases (S_A and S_C, respectively). Series **5** in which the linkages are less polar and more rigid than those of series **4**, display some tilt smectic phases in addition to an N phase, and undergo complicating smectic-smectic transitions.[2)] On the other hand, the series of **1**—**3**, which incorporate both ester and azomethine linkages, are expected to display mesomorphic properties between those two series.

In this paper, we have examined the thermal properties of series **1**—**3**, where a chiral group is introduced at one of the terminal positions, in order to examine the applicability to ferroelectric liquid crystals.

Experimental

Materials. 4-[(*S*)-2-Methylbutoxy]aniline was obtained by the reaction of *p*-nitrophenol and (*S*)-2-methyl-1-bromobutane, followed by catalytic hydrogenation with palladium-carbon. 4-[(*S*)-2-Methylbutoxy]benzoic acid was obtained by the reaction of methyl 4-hydroxybenzoate and (*S*)-2-methyl-1-bromobutane, followed by hydrolysis. 4-(4-*n*-Alkoxybenzoyloxy) and 4-[4-(2-methylbutoxy)benzoyloxy]-benzaldehydes and 4-(4-*n*-alkoxybenzoyloxy)-3-hydroxybenzaldehydes were obtained by the reaction of corresponding acid chlorides and 4-hydroxybenzaldehyde or 2,4-dihydroxybenzaldehyde in dry pyridine. Series **1**—**3** were obtained by the condensation of the corresponding benzaldehydes with the substituted anilines in absolute ethanol. Purification was carried out by recrystallization from absolute ethanol. The purity of the products was confirmed by elementary analysis.

Method: The transition temperatures were determined by using a Nikon POH polarizing microscope fitted with a Mettler FP-5 heating stage, and also a Daini-seikosha SSC-560 differential scanning calorimeter.

Results and Discussion

The transition temperatures and latent heats for series **1**—**3**, are summarized in Tables 1—3.

The S_G^* phase was identified by an examination of the miscibility diagram with *p*-bis(4-*n*-hexylphenyliminomethyl)benzene.[3)]

The series **1** and **2** fundamentally have a similar mesomorphic sequence, i.e., S_G^*-S_C^*-Ch-I, while the

Table 1. Transition Temperatures (°C) and Latent Heats (kJ mol^{-1}) of Series **1**

n	C	S_G^*	S_C^*	Ch	I	$\Delta H_{S_C^*\text{-Ch}}$
3[a)]	. 122.7	—	—	. 222.6	.	—
4[b)]	. 122.2	—	—	. 216.2	.	—
5	. 104.5	—	— 114.2	. 209.1	.	~0
6	. 102.2	(. 82.9)	. 126.5	. 205.3	.	2.4
7	. 85.0	(. 75.5)	. 131.7	. 193.2	.	1.8
8	. 94.0	(. 78.2)	. 144.8	. 197.3	.	2.2
9	. 97.0	(. 74.5)	. 145.2	. 185.6	.	1.7

a) This compound underwent a crystal-crystal transition at 116.5°C. b) This compound underwent a crystal-crystal transition at 119.6°C. Refer to footnote in Table 2.

Table 2. Transition Temperatures (°C) and Latent Heats (kJ mol^{-1}) of Series **2**

n	C	S_G^*	S_C^*	Ch	I	$\Delta H_{S_C^*\text{-Ch}}$
1	. 101.0	—		. 233.3	.	—
2	. 118.6	(. 110.1)	—	. 237.4	.	—
3	. 119.5	(. 118.5)	—	. 218.3	.	—
4	. 113.4	. 116.0	—	. 215.9	.	—
5	. 102.7	(. 101.0)	—	. 205.5	.	—
6	. 92.6	(. 83.5)	. 99.8	. 202.3	.	1.4
7	. 94.5	(. 75.0)	. 111.3	. 196.1	.	1.6
8	. 81.6	(. 76.7)	. 115.9	. 193.6	.	1.4
9	. 91.1	(. 73.5)	. 119.8	. 187.7	.	1.4
10	. 88.6	(. 73.1)	. 122.7	. 184.7	.	1.3

C, S_G^*, S_C^*, Ch, and I represent crystal, smectic G* smectic C*, cholesteric, and isotropic phases, respectively. Parentheses indicate monotropic transitions.

Table 3. Transition Temperatures (°C) and Latent Heats (kJ mol^{-1}) of Series **3**

n	C		S_G^*	S_C^*		Ch		I	$\Delta H_{S_C^*-Ch}$
3	.	133.0	—	—		.	223.6	.	—
4	.	129.8	—	—		.	221.7	.	—
5	.	119.1	—	(.	99.0)	.	208.1	.	~0
6	.	120.5	—	(.	112.4)	.	213.4	.	1.0
7	.	121.9	—	.	122.5	.	210.0	.	2.2
8	.	112.7	—	.	131.3	.	205.2	.	2.2
9	.	113.1	—	.	135.6	.	198.6	.	2.5

thermal stabilities of the mesophases are slightly different. The phase sequence is simpler than those of *p*-bis(4-*n*-alkoxyphenyliminomethyl)benzenes (**5**),[2] and the thermal stability of the S_C^* phase is higher than those of *p*-bis(4-*n*-alkoxyphenoxycarbonyl)benzenes (**4**).[1] The difference in the smectic properties must be concerned with the difference in the geometrical and electrostatic structure, i.e., the cores of **1** and **2** are more rigid but less polar than those of **4**, and more polar but less rigid than **5**.

A noteworthy fact in the two series is that series **1** display a more stable S_C^* phase than **2**. A similar trend has been observed in the thermal properties of some liquid crystals. For example, 4-*n*-alkoxyphenyl 4-[(*S*)-2-methylbutoxy]benzoates do not display an S_C^* phase, while 4-[(*S*)-2-methylbutoxy]phenyl 4-*n*-alkoxybenzoates display it.[4] From these facts, we can assume that a relative orientation of the 2-methylbutoxyl group, a relatively bulky substituent, with respect to the carboxyl group, a polar linkage, is important in determining the thermal stability of the S_C^* phase.

In series **3**, a lateral hydroxy group was introduced in order to increase the chemical stability of the azomethine linkage. Although the mesophase stabilities of **3** are lower than those of series **1** and **2**, probably due to the increased molecular breadth, these appear to have similar mesomorphic properties, while no S_G^* phase could be observed in series **3**.

It is concluded that series **1**—**3** having one ester and one azomethine linkages have simpler smectic polymesomorphism than the corresponding azomethine compounds **5**, and display a higher stable S_C^* phase than the corresponding ester compounds **4**, so that the present series are more useful for dopant liquid crystals for devices employing a ferroelectric mode.

References

1) D. Demus, H. Demus, H. Zaschke, "Flüssig Kristalle im Tabellen', VEB Deutscher Verlag für Grundstoff Industrie," Leipzig (1974).

2) M. E. Neubert and L. J. Maurer, *Mol. Cryst. Liq. Cryst.*, **43**, 313 (1977).

3) A. Wiegelegen, L. Richter, J. Deresch, and D. Demus, *Mol. Cryst. Liq. Cryst.*, **59**, 329 (1980).

4) J. W. Goodby and T. M. Leslie, "Liquid Crystals and Ordered Fluids," ed by A. C. Griffin and J. F. Johnson, Plenum Press, New York (1984), Vol. 4, p. 1.