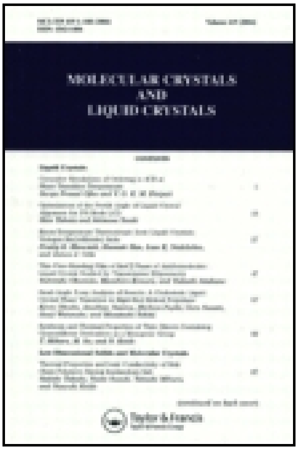


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Occurrence of the Smectic C phase for 3-(2-hydroxy-4-Alkoxybenzylidene-amino)dibenzofurans

Yo Shimizu [a] & Shigekazu Kusabayashi [a]
[a] Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, 565, Japan

Version of record first published: 20 Apr 2011.

To cite this article: Yo Shimizu & Shigekazu Kusabayashi (1986): Occurrence of the Smectic C phase for 3-(2-hydroxy-4-Alkoxybenzylidene-amino)dibenzofurans, Molecular Crystals and Liquid Crystals, 132:3-4, 221-233

To link to this article: http://dx.doi.org/10.1080/00268948608079543

Mol. Cryst. Liq. Cryst., 1986, Vol. 132, pp. 221–233
0026-8941/86/1324–0221/$20.00/0

Occurrence of the Smectic C phase for 3-(2-hydroxy-4-Alkoxybenzylidene-amino)dibenzofurans

YO SHIMIZU and SHIGEKAZU KUSABAYASHI

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

(*Received July 18, 1985*)

The title compounds were investigated on the occurrence of the smectic C phase. Comparison with the geometrical analogues, 3-(2-hydroxy-4-alkoxybenzylideneamino) dibenzothiophenes and 2-(2-hydroxy-4-alkoxybenzylideneamino)fluorenes, indicated that a molecular symmetry favoring the occurrence of the smectic C phase is not always required if the molecule has an appropriate magnitude of the transverse dipole, and that the thermal stability of the smectic C phase (smectic C to smectic A and to nematic phase transition temperatures) of these compounds rises with the increase of the magnitude of transverse dipole moments.

Keywords: smectic C phase, 2-hydroxy-4-alkoxybenzylideneamino derivatives, transverse dipole, dibenzofuran, dibenzothiophene, fluorene

INTRODUCTION

Many studies have so far been made of the structure and the formation of the smectic C phase, and the structure was revealed to be analogous to that of the smectic A phase except for its tilt alignment to the layer normal.[1] Though many factors have been proposed for the occurrence of the smectic C phase, it seems that no definite conclusion has been reached yet.

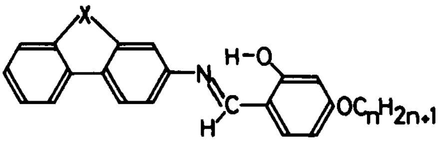
W. L. McMillan proposed that, due to structural factors for the occurrence of the smectic C phase, the molecule should have an approximate center of symmetry, large outboard (antiparallel) dipole moments and a zig-zag (trans) gross shape.[2] A. Wulf also proposed the steric model for the driving force of the tilt alignment, assuming that the molecule is symmetrical and zig-zag shaped.[3]

On the other hand, experimental results which do not agree with the above theories, have been reported. J. W. Goodby et al. have illustrated that the lack of one-side dipole of the two outboard ones does not lead to the disappearance of the smectic C phase, and that branching in the terminal alkyl chain also does not lead to the vanishing of the smectic C phase.[4]

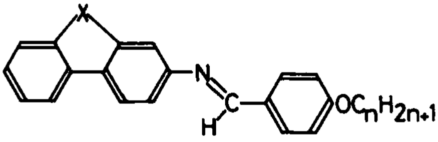
At present, it has been accepted that the favorable factors for the occurrence of the smectic C phase are (1) the appropriate length of the terminal alkyl chain, (2) two terminal alkyl chains at both ends of the core moiety, (3) approximately symmetrical molecular structure and (4) terminal outboard dipole moments.[1]

B. W. Van der Meer et al. have recently emphasized the importance of an acentral transverse dipole for the occurrence of the smectic C phase.[5]

Though it has been observed that the molecule has two alkyl chains at both ends of the core moiety in the majority of compounds showing the smectic C phase, 2-(4-heptyloxybenzylideneamino)fluorenone (**2d**; n = 7) has been found to be a smectic C mesogen.[6] This fluorenone compound has no molecular symmetry and has only one terminal alkyl chain, but a large acentral dipole moment derived from fluorenone moiety. And also 3-(2-hydroxy-4-alkoxybenzylideneamino)-dibenzofurans (**1a**) have been preliminarily reported to be smectic C mesogens with pentyloxy to dodecyloxy derivatives.[7]

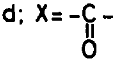


(1)

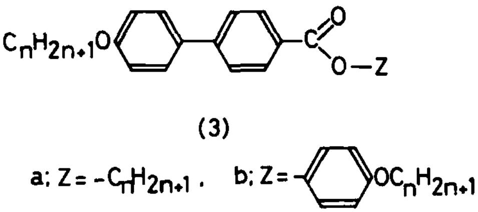


(2)

a; X = -O- , b; X = -S- , c; X = -CH_2-



d; $X = -\underset{\underset{O}{\|}}{C}-$



(3)

In order to study the relation of molecular geometry and molecular dipoles to the occurrence of the smectic C phase in **1a**, 3-(2-hydroxy-4-alkoxybenzylideneamino)dibenzothiophenes (**1b**) and 2-(2-hydroxy-4-alkoxybenzylideneamino)fluorenes (**1c**), the geometrical analogues to **1a**, were prepared and their mesomorphic behavior was investigated.

RESULTS AND DISCUSSION

The mesomorphic behavior of **1a** shows the normal trend for nematic and smectic A phases. As seen in Figure 1, the nematic to isotropic transition temperatures show a normal odd-even alternation and the smectic A to nematic transition temperatures gradually rise as the terminal alkyl chain length increases, leading to the disappearance of the nematic phase in the higher members of the homologous series.

A comparison with 3-(4-alkoxybenzylideneamino)dibenzofurans (**2a**)[8] indicates that the additional hydroxyl group raises the mesomorphic thermal stability by about 30° and that the mesomorphic temperature range is enlarged by about 10°, while the addition does not change the behavior of nematic and smectic A phases in relation to the length of the alkyl chain with regard to the appearance of the smectic A phase and the disappearance of the nematic phase.

On the other hand, it is evident that the lateral hydroxyl group enhances the smectic C thermal stability, leading to the injection of the smectic C phase underlying the smectic A and nematic phases, since the miscibility test indicated that the thermal stability of the smectic C phase (the virtual transition temperatures $T_{S_C-S_A}$) in **2a** seems to be very low, inferred from Figure 2. This smectic C phase was identified by the miscibility test with terephthalylidene-bis-(butylaniline) [TBBA][9], as shown in Figure 3.

The smectic C phase of **1a** appeared in pentyloxy to dodecyloxy derivatives as a monotropic transition except for an enantiotropic octyloxy derivative. The curve of smectic C to nematic or to smectic

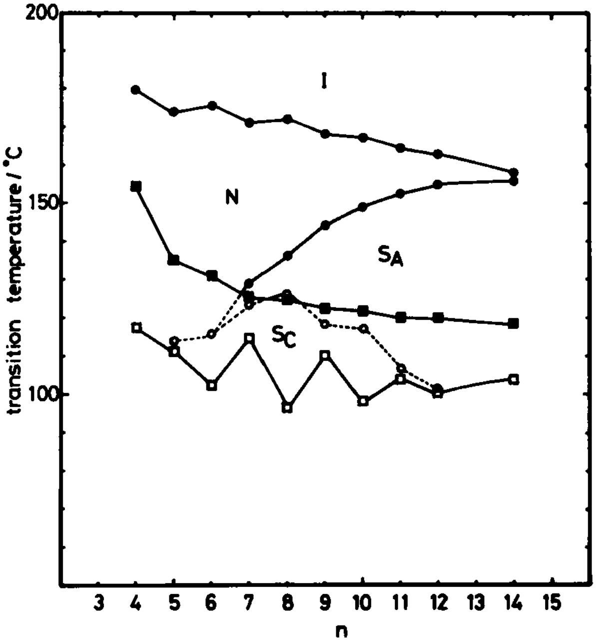


FIGURE 1 Plots of transition temperatures in relation to the number of carbon atoms(n) in the alkyl chain of 3-(2-hydroxy-4-alkoxybenzylideneamino)dibenzofurans **1a**. ●;N-I, ◐;S_A-N, ○;S_C-S_A or N, ■;melting point and □;recrystallization on cooling at 5°C/min.

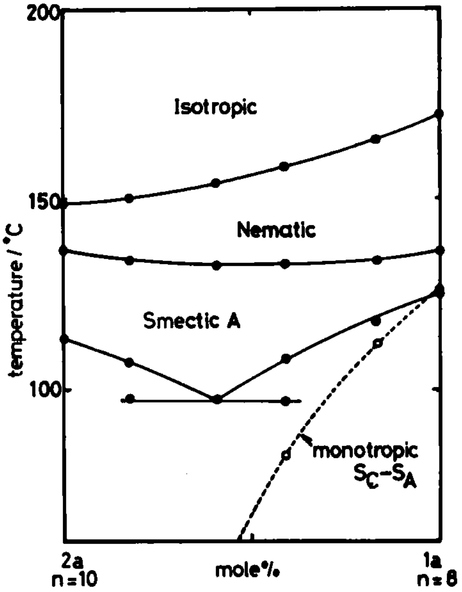


FIGURE 2 A binary phase diagram of **1a**(n = 8) and **2a**(n = 10).

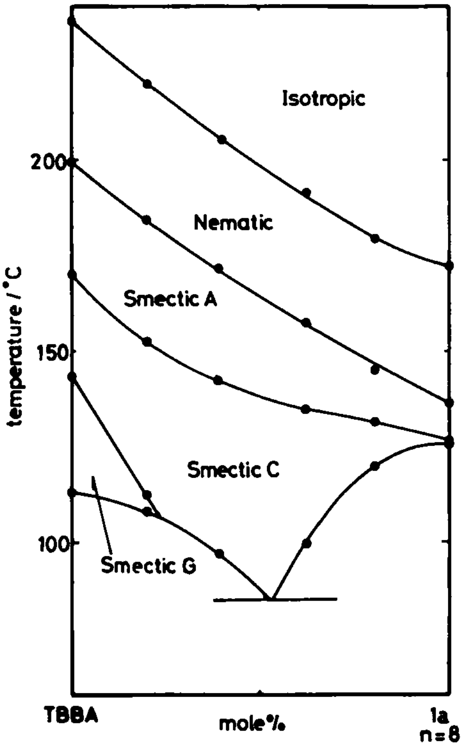


FIGURE 3 A miscibility diagram between **1a**(n = 8) and terephthalylidene-bis-(butylaniline) [TBBA].

A transition temperatures in relation to the number of carbon atoms in the alkyl chain is "parabolic", as G. W. Gray et al. referred to,[10] but is a broader one and reaches maximum with an octyloxy compound. The odd-even alternation of the transition temperatures is ambiguous as compared with that of the biphenyl derivatives having two alkyl chains (**3a** and **3b**).[10]

The microscopic observations of the smectic C phase exhibited two kinds of textures ("Schlieren" and "broken fan") in the homeotropic and homogeneous parts of the smectic A phase on cooling, respectively. However, the smectic C to smectic A transition could not be detected by DSC measurement, probably <0.01kJ/mol., indicating that it is a second-order or a weak first-order phase transition.

The mesomorphic behaviors of **1b** and **1c**, as shown in Figures 4 and 5, also have normal trends in nematic to isotropic and smectic A to nematic phase transitions, like those of **1a**. The narrower temperature width of the odd-even alternation in nematic to isotropic

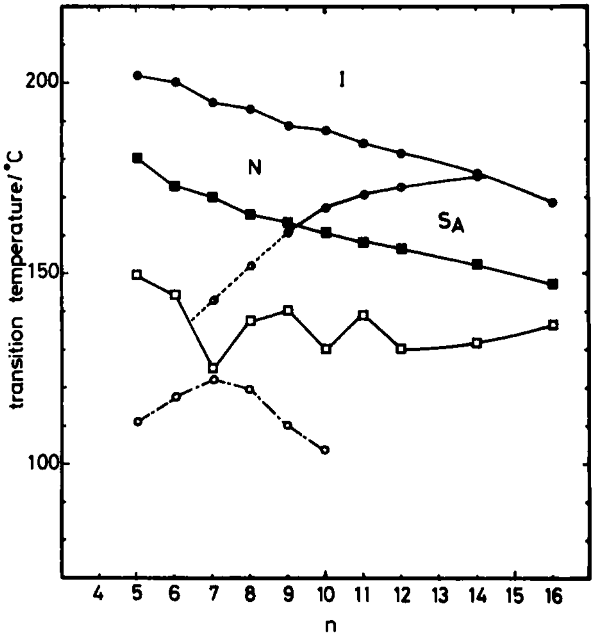


FIGURE 4 Plots of transition temperatures in relation to the number of carbon atoms(n) in the alkyl chain of 3-(2-hydroxy-4-alkoxybenzylideneamino)dibenzothiophenes (**1b**). ●;N-I or S_A-I, ◐;S_A-N, ○;virtual S_C-S_A or N, ■;melting point and □;recrystallization on cooling at 5°C/min.

transition temperatures, rather than that of compounds without a hydroxyl group, is common to **1a**, **1b** and **1c**. This seems to indicate that the molecular interaction among the core moieties in mesophases for **1a**, **1b** and **1c** is stronger than that in non-hydroxyl compounds, thus leading to decreasing the effect of motions of the terminal alkyl chain on the nematic to isotropic transition temperatures.

The compounds **1b** and **1c** show no smectic C phase, similar to the corresponding non-hydroxyl compounds **2b** and **2c**, and the virtual smectic C to smectic A and to nematic phase transition temperatures were estimated by extrapolating the line of smectic C to smectic A or to nematic phase transition temperatures in the binary phase diagram with **1a** possessing the same alkyl chain length as that of the compound to be estimated. Typical diagrams are illustrated in Figure 6.

With **1c**, the virtual smectic C to smectic A transition temperatures are extremely low, while those of **1b** are slightly lower than those of **1a**. Among these three compounds, the difference in the geometrical structure is little,[8] but the dipole moments differ from each other.

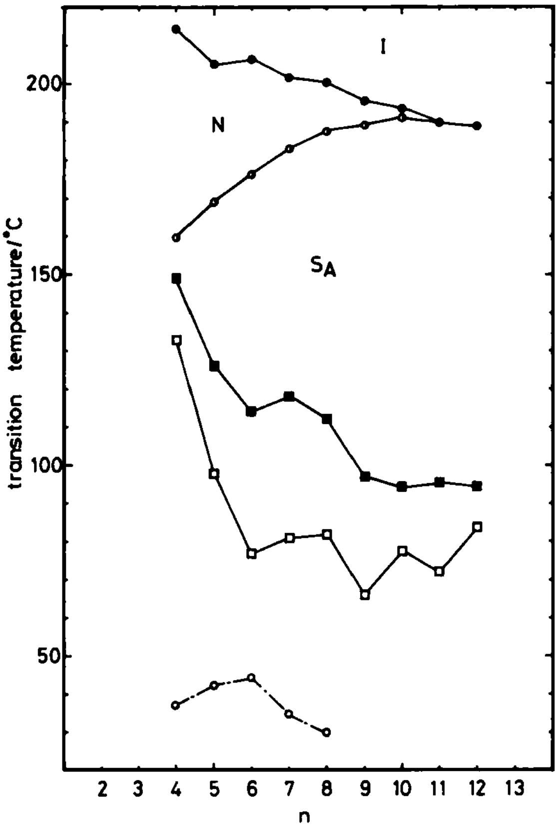


FIGURE 5 Plots of transition temperatures in relation to the number of carbon atoms(n) in the alkyl chain of 2-(2-hydroxy-4-alkoxybenzylideneamino)fluorenes (**1c**). ●;N-I or S_A-I, ◑;S_A-N, ○;virtual S_C-S_A, ■;melting point and □;recrystallization on cooling at 5°C/min.

It has been reported that dibenzofuran, dibenzothiophene and fluorene have electric dipole moments of 0.82D[11], 0.79D[11] and 0.66D[12], respectively, and the directions seem to be along the short axis. Obviously, the order of the magnitude of the dipole moments is the same as that of the thermal stability of the smectic C phase for **1a**, **1b** and **1c**. This fact indicates that the thermal stability of the smectic C phase could be increased by an appropriate magnitude of the transverse dipole, even in such an unsymmetrical molecule. In other words, molecular symmetry is not always required for the occurrence of the smectic C phase if the molecule has an appropriate magnitude of the transverse dipole. Though there remains the possibility that the dipole

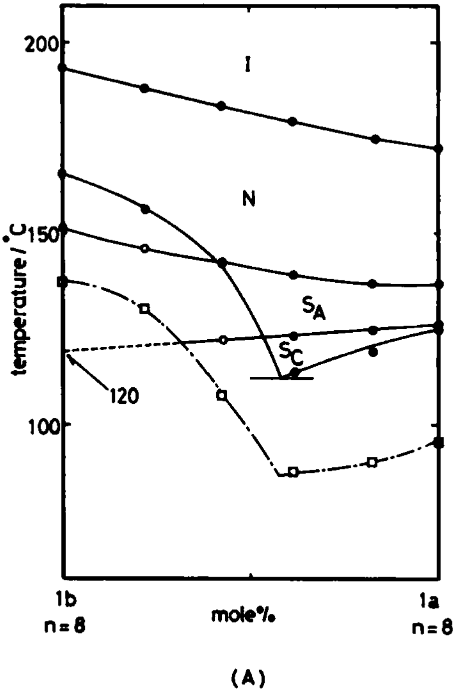
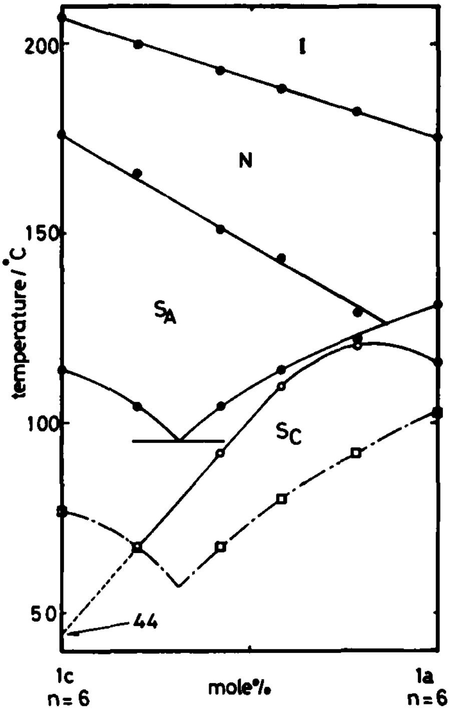


FIGURE 6 Typical binary phase diagrams for the estimation of the virtual S_C-S_A or N transition temperatures. (A) for **1a**(n = 8) and **1b**(n = 8), and (B) for **1a**(n = 6) and **1c**(n = 6). □;recrystallization temperature on cooling at 5°C/min.

moments of dibenzofuran, dibenzothiophene and fluorene work as "outboard" dipoles, the magnitude of "central" dipoles is also an important factor, since **2a**, the non-hydroxyl compounds of **1a**, are considered to have extremely low smectic C thermal stability. This means the magnitude of the dipole moment of azomethine linkage is insufficient for the formation of the smectic C phase at such a high temperature. Considering that compound **2d** (n = 7) is a smectic C mesogen, these results indicate again that an appropriate magnitude of the transverse dipole is required in the core moiety for the formation of the smectic C phase, though the relation of the location of the dipolar part to the smectic C thermal stability is not evident.

As seen in Figures 4 and 5, the positions of the maxima of smectic C thermal stability for **1b** and **1c** are located at n = 7 and n = 6, respectively, and the trend of the curves is also "parabolic".

The "parabolic" shapes of smectic C to smectic A and to nematic phase transition temperatures for **1a**, **1b** and **1c** are intermediate



(B)

FIGURE 6 *continued*

between those of **3a** and **3b**, which are steeper and more gently falling, respectively,[10] in the higher homologues. This might indicate that compounds with only one alkyl chain and compounds whose major dipolar parts are nearer to the terminal alkyl group, are more sensitive to the effect of the alkyl chain length, leading to the importance of dipole-induced dipole interaction[5] for smectic C thermal stability.

EXPERIMENTAL

Measurements of transition temperatures and microscopic observations of textures of mesophases were made using a Nikon polarizing microscope in conjunction with a Mettler FP52 heating stage and FP5 control unit. Transition enthalpies were measured with a Daini Seikosha differential scanning calorimeter, model SSC-560S. ^{1}H-n.m.r. spectra were measured for solutions in $CDCl_3$ with tetramethylsilane as the internal standard with a JNM-PS-100 NMR spectrometer. I.r. spectra were recorded for KBr discs with a Hitachi 215 grating infrared spectrophotometer. Mass spectra were determined with a Hitachi RMV-6T mass spectrometer.

3-(2-Hydroxy-4-alkoxybenzylideneamino)dibenzofurans, 3-(2-hydroxy-4-alkoxybenzylideneamino)dibenzothiophenes and *2-(2-hydroxy-4-alkoxybenzylideneamino)fluorenes* — The azomethines were

TABLE I

Phase transition temperatures (T/°C) of 3-(2-hydroxy-4-alkoxybenzylideneamino)dibenzofurans(**1a**)[b]

n	$T_{C\text{-}S_C,S_A \text{ or } N}$	$T_{S_C\text{-}S_A \text{ or } N}$	$T_{S_A\text{-}N \text{ or } I}$	$T_{N\text{-}I}$	$T_{rec.}$[a]
4	154.5			179.6	117.5
5	135.0	(113.9)[c]		173.9	111.2
6	131.1	(115.7)		175.6	102.5
7	125.6	(123.5)	128.0	171.1	114.6
8	124.8	125.8	136.2	172.0	96.5
9	122.6	(118.4)	144.3	168.3	110.4
10	121.8	(117.3)	149.2	167.6	98.5
11	120.1	(106.6)	152.5	164.3	104.1
12	119.8	(101.6)	154.8	162.7	100.5
14	118.6		156.0	158.1	104.0

[a] C:crystal, S_C:smectic C, S_A:smectic A, N:nematic, I:isotropic and rec.:recrystallization (cooling rate:5°C/min.).

[b] These phase transition temperatures, except for $T_{rec.}$, were reported in the preliminary letter.[7]

[c] ( ):monotropic transition.

TABLE II

Phase transition temperatures (T/°C) of 3-(2-hydroxy-4-alkoxybenzylideneamino)-dibenzothiophenes(**1b**)

n	$T_{C\text{-}S_A \text{ or } N}$	$T_{S_A\text{-}N \text{ or } I}$	$T_{N\text{-}I}$	$T_{rec.}$	$T_{S_C\text{-}S_A \text{ or } N}$(virtual)[a]
5	180.1		201.8	149.5	111
6	172.6		200.2	144.0	118
7	170.0	(143.0)[b]	194.6	126.8	122
8	165.5	(151.7)	193.2	137.5	120
9	163.4	(160.7)	188.7	140.3	110
10	160.3	167.0	187.3	129.8	104
11	157.8	170.4	183.9	139.0	
12	156.7	173.7	181.6	130.5	
14	152.4	175.2	176.2	131.5	
16	147.2	168.6		136.6	

[a] C:crystal, S_C:smectic C, S_A:smectic A, N:nematic, I:isotropic and rec.:recrystallization (cooling rate:5°C/min.).

[b] ( ):monotropic transition.

prepared by refluxing the ethanol solution of 3-aminodibenzofuran, 3-aminodibenzothiophene[13] or 2-aminofluorene and the equimolar 2-hydroxy-4-alkoxybenzaldehyde, and purified by recrystallization from ethanol.

The transition temperatures for **1a**, **1b** and **1c** are listed in Table I, II and III, respectively, and the results of their elemental analyses are given in Table IV, V and VI. The following data for the octyloxy compound are typical of the homologous series as a whole:

For **1a**(n = 8), m/z 415(M^+); ν_{max}. (KBr) 3450, 3060, 2930, 2860, 1620, 1600, 1570, 1405, 1290, 1230, 1120, 835, 820, 740 and 720 cm^{-1}; δ_H($CDCl_3$) 0.89 (3H, t, CH_3), 1.1–2.0 (12H, br m, CH_2CH_2), 3.98 (2H, t, $ArOCH_2R$), 6.47 (1H, d, Ar(5)H), 6.49 (1H, s, Ar(3)H),

TABLE III

Phase transition temperatures (T/°C) of 2-(2-hydroxy-4-alkoxybenzylideneamino)-fluorenes(**1c**)

n	$T_{C\text{-}S_A \text{ or } N}$	$T_{S_A\text{-}N \text{ or } I}$	$T_{N\text{-}I}$	T_{rec}	$T_{S_C\text{-}S_A}$ (virtual)[a]
4	149.3	159.6	214.5	133.0	37
5	126.3	169.1	205.0	97.9	42
6	114.0	176.4	206.6	77.0	44
7	118.3	183.2	201.7	80.8	34.5
8	112.2	187.6	200.5	81.8	29.5
9	97.0	189.0	195.6	66.2	
10	94.4	190.8	193.6	77.5	
11	95.4	189.9		72.1	
12	94.5	188.9		83.7	

[a] C:crystal, S_C:smectic C, S_A:smectic A, N:nematic, I:isotropic and rec.:recrystallization (cooling rate:5°C/min.).

TABLE IV

Elemental analyses for 3-(2-hydroxy-4-alkoxybenzylideneamino)dibenzofurans(**1a**)

	Found(%)			Molecular	Required(%)		
n	C	H	N	formula	C	H	N
4	76.75	5.87	3.84	$C_{23}H_{21}NO_3$	76.86	5.89	3.90
5	77.12	6.22	3.74	$C_{24}H_{23}NO_3$	77.18	6.21	3.77
6	77.54	6.38	3.59	$C_{25}H_{25}NO_3$	77.49	6.50	3.61
7	77.81	6.75	3.55	$C_{26}H_{27}NO_3$	77.78	6.78	3.49
8	77.86	6.99	3.44	$C_{27}H_{29}NO_3$	78.04	7.03	3.37
9	78.18	7.16	3.23	$C_{28}H_{31}NO_3$	78.29	7.27	3.26
10	78.38	7.46	3.08	$C_{29}H_{33}NO_3$	78.52	7.50	3.16
11	78.68	7.68	3.05	$C_{30}H_{35}NO_3$	78.74	7.71	3.06
12	78.79	7.91	2.83	$C_{31}H_{37}NO_3$	78.95	7.91	2.97
14	79.32	8.28	2.77	$C_{33}H_{41}NO_3$	79.32	8.27	2.80

TABLE V

Elemental analyses for 3-(2-hydroxy-4-alkoxybenzylideneamino)dibenzothiophenes (**1b**)

n	Found(%) C	H	N	S	Molecular formula	Required(%) C	H	N	S
5	73.94	5.83	3.50	8.24	$C_{24}H_{23}NO_2S$	74.01	5.95	3.60	8.23
6	74.12	6.30	3.35	7.97	$C_{25}H_{25}NO_2S$	74.41	6.24	3.47	7.94
7	74.87	6.51	3.33	7.70	$C_{26}H_{27}NO_2S$	74.79	6.52	3.35	7.68
8	75.09	6.76	3.27	7.43	$C_{27}H_{29}NO_2S$	75.14	6.77	3.25	7.43
9	75.32	7.02	3.18	7.14	$C_{28}H_{31}NO_2S$	75.47	7.01	3.14	7.19
10	75.81	7.34	2.93	7.09	$C_{29}H_{33}NO_2S$	75.78	7.24	3.05	6.97
11	75.85	7.52	2.83	6.80	$C_{30}H_{35}NO_2S$	76.07	7.45	2.96	6.77
12	76.23	7.78	2.73	6.53	$C_{31}H_{37}NO_2S$	76.35	7.65	2.87	6.57
14	76.59	8.19	2.58	6.20	$C_{33}H_{41}NO_2S$	76.85	8.01	2.72	6.22
16	77.32	8.66	2.40	5.60	$C_{35}H_{45}NO_2S$	77.30	8.34	2.58	5.90

TABLE VI

Elemental analyses for 2-(2-hydroxy-4-alkoxybenzylideneamino)fluorenes(**1c**)

n	Found(%) C	H	N	Molecular formula	Required(%) C	H	N
4	80.49	6.46	3.85	$C_{24}H_{23}NO_2$	80.64	6.49	3.92
5	80.87	6.79	3.72	$C_{25}H_{25}NO_2$	80.83	6.78	3.77
6	80.75	6.99	3.63	$C_{26}H_{27}NO_2$	81.01	7.06	3.63
7	80.92	7.30	3.50	$C_{27}H_{29}NO_2$	81.17	7.32	3.51
8	81.00	7.48	3.35	$C_{28}H_{31}NO_2$	81.32	7.56	3.39
9	81.29	7.76	3.23	$C_{29}H_{33}NO_2$	81.46	7.78	3.28
10	81.21	7.96	3.18	$C_{30}H_{35}NO_2$	81.59	7.99	3.17
11	81.61	8.18	3.09	$C_{31}H_{37}NO_2$	81.71	8.18	3.07
12	81.59	8.38	3.03	$C_{32}H_{39}NO_2$	81.84	8.37	2.98

7.1–7.7 (6H, m), 7.90 (2H, d, dibenzofuran (1 and 9)H), 8.57 (1H, s, CH=N) and 13.62 (1H, s, OH).

For **1b** (n = 8), m/z 431 (M^+); ν_{max}. (KBr) 3450, 3050, 2920, 2850, 1620, 1585, 1565, 1400, 1290, 1230, 1185, 810 and 730 cm^{-1}; $\delta_H(CDCl_3)$ 0.89 (3H, t, CH_3), 1.1–2.0 (12H, br m, CH_2CH_2), 3.98 (2H, t, $ArOCH_2R$), 6.47 (1H, d, Ar(5)H), 6.50 (1H, s, Ar(3)H), 7.1–7.6 (4H, m), 7.69 (1H, s, dibenzothiophene(3)H), 7.76–7.94 (1H, m), 8.57 (1H, s, CH=N) and 13.63 (1H, s, OH).

For **1c** (n = 8), m/z 413(M^+); ν_{max}. (KBr) 3450, 3055, 2935,j 2860, 1630, 1600, 1570, 1455, 1405, 1305, 1235, 1175, 1145, 735 and 725 cm^{-1}; $\delta_H(CDCl_3)$ 0.89 (3H, t, CH_3), 1.1–2.0 (12H, br m, CH_2CH_2), 3.91 (2H, s, fluorene-CH_2), 3.98 (2H, t, $ArOCH_2R$), 6.48 (1H, d, Ar(5)H), 6.51 (1H, s, Ar(3)H), 7.1–7.6(6H, m), 7.76 (2H, d, fluorene(4 and 5)H), 8.56 (1H, s, CH=N) and 13.86 (1H, s, OH).

Acknowledgment

This work was in part supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1. G. W. Gray and J. W. Goodby, "*Smectic Liquid Crystals — Textures and Structures*", Leonard Hill, Glasgow and London, 1984.
2. W. L. McMillan, *Phys. Rev. A*, 1973, **8**, 1921.
3. A. Wulf, *Phys. Rev. A*, 1975, **11**, 365.
4. J. W. Goodby, G. W. Gray and D. G. McDonnell, *Mol. Cryst. Liq. Cryst. Lett.*, 1977, **34**, 183.
5. B. W. Van der Meer and G. Vertogen, *J. Phys. (Paris) Colloq.*, 1979, **40**, C3-222.
6. G. Sigaud, F. Hardouin and M. F. Achard, *Solid State Commun.*, 1977, **23**, 35. This compound was originally reported by G. W. Gray et al. (G. W. Gray, J. B. Hartley, A. Ibbotson and B. Jones, *J. Chem. Soc.*, 1955, 4359.), but they did not classify the smectic type at that time.
7. Y. Shimizu and S. Kusabayashi, *Chem. Lett.*, 1985, 1003.
8. Y. Shimizu, A. Ikegami, M. Nojima and S. Kusabayashi, *Mol. Cryst. Liq. Cryst.*, in press.
9. D. Demus, J. W. Goodby, G. W. Gray and H. Sackmann, *Mol. Cryst. Liq. Cryst. Lett.*, 1980, **56**, 311.
10. G. W. Gray and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 1976, **37**, 157.
11. T. Nagai, Y. Koga, H. Takahashi and K. Higasi, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 1022. These values were changed to the Debye unit from the original unit (C m).
12. V. Baliah and M. Krishna Pillay, *Ind. J. Chem.*, 1971, **9**, 563.
13. R. K. Brown, R. G. Christiansen and R. B. Sandin, *J. Am. Chem. Soc.*, 1948, **70**, 1748; W. Tagaki, K. Kikukawa, K. Ando and S.Oae, *Chem. Ind.*, 1964, 1624.