

Liquid Crystallinity of 2-Fluorenyl 4-Alkylbenzoates

Jun Yamamoto, Takao Kimura, Yutaka Takabayashi,[1] Toru Oba, Michinori Karikomi, and Masahiro Minabe*

Department of Applied Chemistry, Faculty of Engineering, Utsunomiya University, Yoto 7-1-2, Utsunomiya 321-8585

[1]Research Institute of Scientific Crime Detection, Tochigi Police, Hanawada 1-1-20, Utsunomiya 320-8510

Received August 26, 2004; E-mail: minabe@cc.utsunomiya-u.ac.jp

The liquid crystallinity values of 2-fluorenyl 4-alkyl (pentadecyl, *n*-, or *s*-butyl)-benzoates were compared with those of biphenyl homologues. Cyano group or hydrogen was used as the end group at the 7-position of 2-fluorenol moiety. Methoxy and hydroxy groups in addition to hydrogen were examined as a lateral substituent at the 2-position of 4-alkylbenzoic acid unit. 7-Cyano-2-fluorenyl 2-hydroxy-4-pentadecylbenzoate shows very similar properties to those of 4′-cyanobiphenyl-4-yl 2-hydroxy-4-pentadecylbenzoate.

This paper compares the liquid crystallinity values of 2-fluorenyl 4-alkylbenzoates with those of biphenyl homologues. Many fluorene derivatives have been studied in the field of thermotropical liquid crystals.[1–4] Study on a luminescent mesogen is one of the recent developments of a functional design in this field.[5] A liquid crystal that includes fluorene as a mesogen unit has both merits and demerits, comparing to the corresponding biphenyl derivatives which are widely used at present.[6] Fluorene is coplanar, but biphenyl is not. Therefore, one of the merits of fluorene as a core is that thermal stability of the liquid crystal phase is expected to be superior to biphenyl by increasing polarity due to the delocalization of π-electrons over the biphenyl moiety. One of the demerits of fluorene is that the methylene group increases the molecular width. In addition, each substituent at the 2- and 7-positions deviates by an angle of 12° from the axis of the central 4a–4b bond. The molecule of 2,7-disubstituted fluorene that is easily obtained by the electrophilic substitution thus has a banana shape.[7,8] These derivatives decrease the thermal stability of the liquid crystal phase.

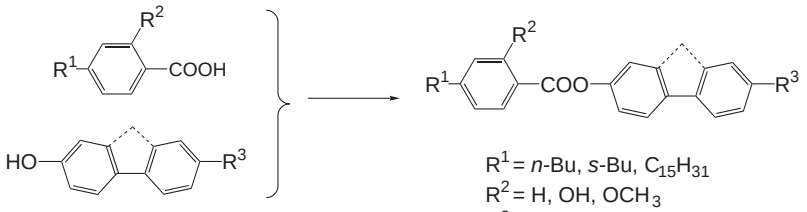
The connector examined in this paper is an ester group formed by the combination of 2-fluorenol (or biphenyl-4-ol) with 4-alkylbenzoic acid, as is shown in Scheme 1. The ester group is easily formed and the polar ester scarcely affects the temperature range and the clearing point in liquid crystallinity.[9]

The terminal group of liquid crystals plays an important role in the liquid crystallinity. In this study, *n*-butyl, *s*-butyl, or pentadecyl group is examined as an alkyl end at the 4-alkylbenzoic acid moiety. One of reactants is obtained from 3-pentadecylphenol, a cardanol[10] that is derived from nuts of *Anacardium occidentale L.* This compound is used as one of starting materials of phenol resin and is expected to develop more valuable usage of the biomass.[11] The other terminal end, or the 7-position of the 2-fluorenol moiety, is occupied by hydrogen or a polar cyano group. In the case of hydrogen, fluorene itself is a polar terminal cap in which the delocalized aromatic ring should increase the polarity and the hardness of the molecule, compared to those of biphenyl.

This paper deals with the influence of the cross effects due to the molecular structure described above. The counteracting of these opposing effects should result in the liquid crystallinity of 2-fluorenyl 4-alkylbenzoates being similar and/or superior to that of biphenyl homologues. The findings should be of help to design new liquid crystals or to modify authentic biphenyl-type liquid crystals.

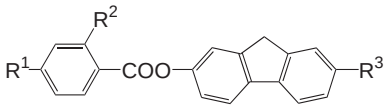
Results and Discussion

The target esters, **1**–**18**, were obtained by the reactions of the corresponding alcohol (**19**–**22**) with the acid chloride derived from 4-alkylbenzoic acid (**23**–**27**), in the presence of triethylamine in chloroform (Scheme 2). The precursor, 7-cyano-2-fluorenol (**20**), was synthesized from 7-bromo-2-fluorenol[12] via acetylation of hydroxy group and substitution of bromine atom by cyano group.[13] Carboxylic acid **23** was derived from 2′-hydroxy-4′-pentadecylacetophenone[14] by bromoform reac-



Scheme 1.

Published on the web March 11, 2005; DOI 10.1246/bcsj.78.523



1 ($R^1 = C_{15}H_{31}$, $R^2 = OCH_3$, $R^3 = H$)

2 ($R^1 = C_{15}H_{31}$, $R^2 = OH$, $R^3 = H$)

3 ($R^1 = C_{15}H_{31}$, $R^2 = R^3 = H$)

4 ($R^1 = n\text{-}C_4H_9$, $R^2 = R^3 = H$)

5 ($R^1 = s\text{-}C_4H_9$, $R^2 = R^3 = H$)

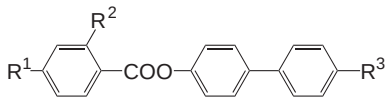
6 ($R^1 = C_{15}H_{31}$, $R^2 = OCH_3$, $R^3 = CN$)

7 ($R^1 = C_{15}H_{31}$, $R^2 = OH$, $R^3 = CN$)

8 ($R^1 = C_{15}H_{31}$, $R^2 = H$, $R^3 = CN$)

9 ($R^1 = n\text{-}C_4H_9$, $R^2 = H$, $R^3 = CN$)

10 ($R^1 = s\text{-}C_4H_9$, $R^2 = H$, $R^3 = CN$)



11 ($R^1 = C_{15}H_{31}$, $R^2 = OCH_3$, $R^3 = H$)

12 ($R^1 = C_{15}H_{31}$, $R^2 = OH$, $R^3 = H$)

13 ($R^1 = C_{15}H_{31}$, $R^2 = R^3 = H$)

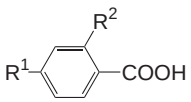
14 ($R^1 = C_{15}H_{31}$, $R^2 = OCH_3$, $R^3 = CN$)

15 ($R^1 = C_{15}H_{31}$, $R^2 = OH$, $R^3 = CN$)

16 ($R^1 = C_{15}H_{31}$, $R^2 = H$, $R^3 = CN$)

17 ($R^1 = n\text{-}C_4H_9$, $R^2 = H$, $R^3 = CN$)

18 ($R^1 = s\text{-}C_4H_9$, $R^2 = H$, $R^3 = CN$)



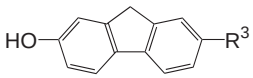
23 ($R^1 = C_{15}H_{31}$, $R^2 = OCH_3$)

24 ($R^1 = C_{15}H_{31}$, $R^2 = OH$)

25 ($R^1 = C_{15}H_{31}$, $R^2 = H$)

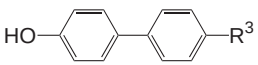
26 ($R^1 = n\text{-}C_4H_9$, $R^2 = H$)

27 ($R^1 = s\text{-}C_4H_9$, $R^2 = H$)



19 ($R^3 = H$)

20 ($R^3 = CN$)



21 ($R^3 = H$)

22 ($R^3 = CN$)

Scheme 2.

tion after protection of hydroxy group by methylation. Compound **23** was converted to **24** via demethylation. 4-Pentadecylbenzoic acid (**25**)[15] was synthesized from pentadecylbenzene through acetylation and successive bromoform reaction, and it shows a smectic phase between 98 and 107 °C.

The structures of **1**–**18** were confirmed based on their spectral analyses. The thermal behavior was determined at the second heating and/or cooling process using a polarized microscope and a DSC apparatus, as is summarized in Table 1. In brief, a smectic phase was observed in the case of nitrile compounds attached by pentadecyl group as the R^1 of the acid moiety. On the other hand, a nematic phase was confirmed in the nitrile derivatives attached by *n*- or *s*-butyl group as the R^1. A nematic phase was also observed within a narrow temperature range in the case of fluorene derivatives, **2** and **3**, in which pentadecyl group was attached as the R^1.

Introduction of a cyano group as the R^3 group results in increasing thermal stability of liquid crystal. This finding is due to larger dipole moment and stronger electron-withdrawing property of the cyano group, compared to those of hydrogen. These effects affect the molecules themselves to increase the intermolecular attraction, and consequently to elevate the clearing point (M–I).[16] The melting points of **9** and **16** look abnormal, being a little lower than those of the mother **4**[3] and **13**, respectively.

The lateral substituent, R^2 (OCH_3, OH, or H), was examined using the following three series: **1**/**2**/**3**, **6**/**7**/**8**, and **14**/**15**/**16**. The melting point (C–M) of these series increases in the order of OH < OCH_3 < H. On the other hand, the clearing point (M–I) is higher in the order of OCH_3 < OH < H. The order of the clearing point fits with the melting points (C–I) of the series, **11**, **12**, and **13**, which do not show liquid crystallinity.

Figure 1 shows the optimum structural models of **6** and **15**. The widest part of **6** is between the methoxy group and the H_5 of acid moiety (ca. 0.66 nm). The distance (ca. 0.53 nm) between the H_9 and H_4(5) of fluorene part is the widest part of **8**. The intermolecular force maintaining the liquid crystal state decreases with increasing width of molecule.[17] The methoxy derivatives **6** and **14** lowers the interaction between mesogen units and hence lowers their clearing points.

The distance between the hydroxy group and the H_5 of salicylic moiety of **7** is estimated to be ca. 0.53 nm, similar to the distance between the H_9 and H_4(5) of fluorene part. The IR spectra of hydroxy compounds, or **2**, **7**, **12**, and **15**, show strong intramolecular hydrogen bonds between the hydroxy hydrogen and the carbonyl oxygen of salicylic moiety, as is supported by ab initio calculations. This disturbs the rotation between the phenyl carbon and the carbonyl carbon in salicylic

Table 1. Phase-Transition Temperature of Compounds **1**–**18**

Compd	Core[a)]	R^1	R^2	R^3	Phase-transition temp.[b)]/°C	Yield/%
1	Fluo	$C_{15}H_{31}$	OCH_3	H	C–86–I	47
2	Fluo	$C_{15}H_{31}$	OH	H	C–83 [35.5]–N–87 [0.4]–I	63
3	Fluo	$C_{15}H_{31}$	H	H	C–106 [36.9]–N–108 [0.5]–I	87
4	Fluo	*n*-C_4H_9	H	H	C–135–I	69
5	Fluo	*s*-C_4H_9	H	H	C–106–I	65
6	Fluo	$C_{15}H_{31}$	OCH_3	CN	C–105 [48.9]–S–111 [2.6]–I	58
7	Fluo	$C_{15}H_{31}$	OH	CN	C–83 [34.0]–S–153 [3.0]–I	54
8	Fluo	$C_{15}H_{31}$	H	CN	C–128 [33.0]–S–192 [4.1]–I	62
9	Fluo	*n*-C_4H_9	H	CN	C–132 [22.0]–N–221 [0.3]–I	78
10	Fluo	*s*-C_4H_9	H	CN	C–131 [21.0]–N–134[c)]–I	66
11	Biph	$C_{15}H_{31}$	OCH_3	H	C–58–I	44
12	Biph	$C_{15}H_{31}$	OH	H	C–78–I	17
13	Biph	$C_{15}H_{31}$	H	H	C–95–I	81
14	Biph	$C_{15}H_{31}$	OCH_3	CN	C–87 [48.6]–S–126 [3.5]–I	54
15	Biph	$C_{15}H_{31}$	OH	CN	C–84 [53.7]–S–153 [3.8]–I	65
16	Biph	$C_{15}H_{31}$	H	CN	C–92 [38.5]–S–194 [4.9]–I	88
17	Biph	*n*-C_4H_9	H	CN	C–95 [19.2]–N–244 [0.5]–I	79
18	Biph	*s*-C_4H_9	H	CN	C–117 [20.0]–N–171 [0.2]–I	83

a) Fluo: Fluorene; Biph: biphenyl. b) C: Crystal phase; I: isotropic phase; S: smectic phase; N: nematic phase. Kind of smectic phases is uncertain at present. []: Enthalpy change at heating process (kJ mol^{-1}). c) No change was observed on the DSC curve.

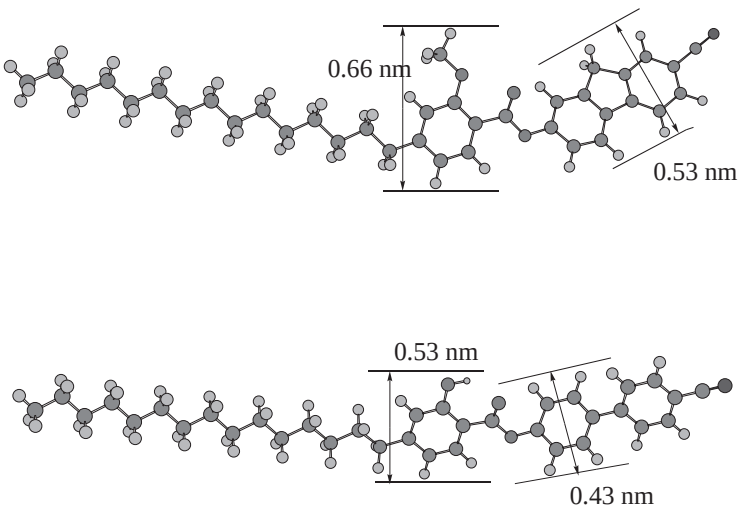


Fig. 1. Optimum structural models of **6** (upper) and **15** (lower).

moiety. These result in lowering of the melting point and widening the thermal stability of liquid crystal phase in the cases of **2** and **7**, compared to the cases of **3** and **8**, respectively. On the other hand, the width at the biphenyl moiety in **15** and **16** is only ca. 0.43 nm, narrower than that of salicylic part. Therefore, the presence of hydroxy group in **15** seems to decrease the thermal stability compared to that of **16**, despite the lower melting point.

The terminal substitent at the R^1 examined here is pentadecyl, *n*- or *s*-butyl group. In the case that the R^3 was cyano group, a smectic phase was observed when pentadecyl group was used as the R^1, and a nematic phase appeared when *n*- or *s*-butyl was attached. These findings have been generalized as the relation between the length of the alkyl terminal chain and the species of liquid crystal phase.[18] The effect of the R^1 is compared in the following two series: **8**/**9**/**10** and **16**/**17**/**18**. The temperature range of liquid crystal phase increases in the order of *s*-butyl < pentadecyl < *n*-butyl. Lower clearing points of **8** and **16** compared to those of **9** and **17** are explained by the consideration that longer alkyl chain increases the mobility of the molecules and increases the overall entropy. The narrower range of *s*-butyl compounds (**10**, **18**) than that of *n*-butyl derivatives (**9**, **17**) is due to the fact that the *s*-butyl group is wider than *n*-butyl group as a terminal substitent.

The endothermic peak at N–I transition could not observed on the DSC curve of **10**. The enthalpy change at N–I transition is, in general, small because of the low order of molecules. This tendency should be emphasized by the bent structure as fluorene derivatives.[5]

A short range of nematic phase was detected in fluorene series, **2** and **3**, but was not observed in the corresponding biphenyl derivatives, **12** and **13**. In these cases, fluorene (or biphenyl)

itself acts as a polar terminal end as well as a mesogen unit. The polarity value of fluorene is higher than that of biphenyl; this is due to the delocalization of π-electrons and results in increasing of the intermolecular attraction.

The mesogen unit of cyanofluorene series, **6**–**10**, is compared with that of cyanobiphenyl series, **14**–**18**. The 9-methylene group of fluorene elevates their melting points because of increasing molecular weight and of wider coplanarity, compared to the melting points of biphenyl. Also, the 9-methylene group increases the width and the forced bent structure of the mesogen unit. These decrease the range of liquid crystal phase, compared to the case of biphenyl series.[19,20]

Compound **7** is very similar to **15** as a liquid crystal, though the molecular arrangement of **7** may be a little more random than that of **15**, as observation of their enthalpy changes indicates. These findings should be valuable for design of new liquid crystals or modification of authentic liquid crystals by transformation of substituents.

Experimental

The melting points are uncorrected. The NMR ($CDCl_3$) and IR (KBr pellets) spectra were recorded with a Varian VXR-300 and with a JASCO FT/IR-430, respectively. The DSC curves were obtained with a DSC-3200S (Mac Science Co.) at scanning rate of 5 °C/min under nitrogen atmosphere (100 mL/min). The elemental analyses and mass spectra were measured with an EA 1108 CHNS-O (Fison Instruments) and with a JMX-AX 500 (JEOL, 70 eV), respectively.

The conformation of the molecules was estimated using a molecular-mechanics program in Chem 3D pro (CambridgeSoft Corp.) on an iMac (Macintosh). The molecular structure of the fluorenyl mesogen part was also examined by ab initio calculation (HyperChem release 7.5, Hypercube Inc.). The octadecyl group of **7** was replaced with a methyl group in silico for simplicity, and the molecular structure of this model compound, 7-cyano-2-fluorenyl 2-hydroxy-4-methylbenzoate, was energy-minimized by molecular mechanics (MM+) and then by molecular orbital methods (PM3). Further optimization was carried out at the MP2/6-31G$^+$ level starting from the PM3 geometry. The finally obtained structure of the model molecule was found to be nearly the same as those obtained by PM3 and MM+ calculations.

7-Cyano-2-fluorenol (20). Upon acetylation of 7-bromo-2-fluorenol[12] (yield 91%, mp 128–130 °C), the ester (9.09 g, 30 mmol) was added to a freshly-prepared mixture of copper(I) cyanide (4.03 g, 45 mmol) in *N*-methyl-2-pyrrolidone (130 mL), and the whole was refluxed for 2.5 h according to the method mentioned elsewhere.[13] The resulting mixture was treated with iron(III) chloride (7.29 g, 45 mmol) and 3 M HCl (180 mL) at 85 °C for 1.5 h, and extracted with toluene, giving 5.11 g (82%) of **20**: Mp 222–225 °C (from 50% ethanol); IR 3520–3160 (OH), 2230 cm^{-1} (CN); ^{1}H NMR δ 3.90 (2H, s, H_9), 5.07 (1H, s, OH), 6.91 (1H, dd, $J = 8.4$, 2.1 Hz, H_3), 7.06 (1H, s, H_1), 7.64 (1H, d, $J = 8.1$ Hz, H_6), 7.69 (1H, d, $J = 8.4$ Hz, H_4), 7.73 (1H, d, $J = 8.1$ Hz, H_5), 7.76 (1H, s, H_8); MS m/z 207 (M^+). Anal. Found: C, 80.99; H, 3.96; N, 6.68%. Calcd for $C_{14}H_9NO$: C, 81.14; H, 4.38; N, 6.76%.

2-Hydroxy-4-pentadecylbenzoic Acid (24). 2′-Hydroxy-4′-pentadecylacetophenone[14] (6.92 g, 20 mmol) was treated with dimethylsulfate (6.57 mL, 52 mmol) and potassium hydroxide (3.76 g) in acetone (50 mL) for 7 h at room temperature. Upon filtration of the mixture, the filtrate afforded 6.55 g (91%) of 2′-methoxy-4′-pentadecylacetophenone: Mp 47–49 °C (from ethanol): IR 1660 cm^{-1} (CO). A solution of 2′-methoxy-4′-pentadecylacetophenone (5.40 g, 15 mmol) in dioxane (100 mL) was added to a sodium hypobromite solution obtained from bromine (4.61 mL, 90 mmol) and sodium hydroxide (10.0 g, 250 mmol) in water (90 mL) at 0 °C for 1 h. After stirring for 20 h at room temperature, 4.94 g (91%) of 2-methoxy-4-pentadecylbenzoic acid (**23**) was isolated by a usual treatment: Mp 77–79 °C (from 80% ethanol): IR 3400–2400 (OH), 1710 cm^{-1} (CO).

A mixture of **23** (2.17 g, 6.0 mmol) and phosphorus (red, 3.0 g) in acetic anhydride (30 mL) was stirred with hydroiodic acid (55%, 30 mL, 22.8 mmol) at 95 °C for 5 h. Upon a usual treatment, 1.76 g (85%) of **24** was isolated: Mp 95–97 °C (from 80% ethanol); IR 3400–2400 (COOH), 3240 (OH), 1650 cm^{-1} (CO); ^{1}H NMR δ 0.88 (3H, t, $J = 6.8$ Hz, Me), 1.20–1.40 (24H, m), 1.62 (2H, q, $J = 7.5$ Hz), 2.61 (2H, t, $J = 7.5$ Hz), 6.76 (1H, dd, $J = 8.4$, 1.5 Hz, H_5), 6.82 (1H, d, $J = 1.5$ Hz, H_3), 7.80 (1H, d, $J = 8.4$ Hz, H_6), 10.40 (1H, s, OH).

4-Pentadecylbenzoic Acid (25). 4′-Pentadecylacetophenone was obtained by the Friedel-Carfts reaction of pentadecylbenzene with acetyl chloride and aluminum chloride in carbon disulfide in a 68% yield: Mp 41–43 °C (from ethanol); IR 1680 cm^{-1} (CO). Compound **25** was derived from 4′-pentadecylacetophenone by a method similar to that used above in a 89% yield: Phase-transition temperature C–98 °C [enthalpy change, 23.4 kJ/mol]–s–107 °C [7.3 kJ/mol]–I (from 80% ethanol) (lit[15] mp 97–98 °C); IR 3160–2360 (OH), 1680 cm^{-1} (CO); ^{1}H NMR δ 0.88 (3H, t, $J =$ 6.6 Hz, Me), 1.20–1.40 (24H, m), 1.63 (2H, q, $J = 7.5$ Hz), 2.67 (2H, t, $J = 7.5$ Hz), 7.28 (2H, d, $J = 8.4$ Hz, $H_{3,5}$), 8.02 (2H, d, $J = 8.4$ Hz, $H_{2,6}$); MS m/z 332 (M^+). Anal. Found: C, 79.40; H, 11.16%. Calcd for $C_{22}H_{36}O_2$: C, 79.46; H, 10.92%.

2-Fluorenyl 2-Methoxy-4-pentadecylbenzoate (1). Typical Procedure: Acid **23** (0.72 g, 2.0 mmol) in thionyl chloride (20 mL) was stirred at 50–60 °C for 1 h and then at 85 °C for 3.5 h. Evaporation of the excess thionyl chloride in vacuo gave the corresponding acid chloride: IR 1780 cm^{-1}.

The acid chloride was added dropwise with stirring to a mixture of **19** (0.54 g, 3.0 mmol) and triethylamine (0.42 g, 4.2 mmol) in chloroform (40 mL) below 5 °C, and the whole was stirred for 1 h. After treatment with 3 M HCl and then water, the solution was dried over anhydrous sodium sulfate, evaporated in vacuo, and the residue was chromatographed on silica gel with cyclohexane/benzene (1/4). The crude ester was recrystallized from ethanol, affording 0.50 g (47%) of **1**: Mp 86–88 °C; IR 1740 cm^{-1} (CO); ^{1}H NMR δ 0.88 (3H, t, $J = 6.6$ Hz, Me), 1.20–1.40 (24H, m), 1.66 (2H, q, $J = 7.8$ Hz), 2.67 (2H, t, $J = 7.8$ Hz), 3.92 (2H, s, $H_{9'}$), 3.95 (3H, s, OMe), 6.85 (1H, s, H_3), 6.88 (1H, dd, $J = 8.1$, 1.5 Hz, H_5), 7.22 (1H, dd, $J = 8.1$, 2.1 Hz, $H_{3'}$), 7.30 (1H, td, $J = 7.5$, 2.1 Hz, $H_{7'}$), 7.38 (1H, t, $J = 7.5$ Hz, $H_{6'}$), 7.41 (1H, s, $H_{1'}$), 7.54 (1H, d, $J = 7.5$ Hz, $H_{8'}$), 7.77 (1H, d, $J =$ 7.5 Hz, $H_{5'}$), 7.79 (1H, d, $J = 8.1$ Hz, $H_{4'}$), 7.99 (1H, d, $J = 7.8$ Hz, H_6); ^{13}C NMR δ 14.1, 22.7, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 31.1, 31.9, 36.4, 37.0 ($C_{9'}$), 56.0 (OMe), 112.4 (C_3), 116.4 (C_1), 118.9 ($C_{1'}$), 119.8 ($C_{5'}$), 120.3 ($C_{4'}$), 120.4 (C_5), 120.5 ($C_{3'}$), 125.0 ($C_{8'}$), 126.5 ($C_{7'}$), 126.8 ($C_{6'}$), 132.4 (C_6), 139.3 ($C_{4'a}$), 141.1 ($C_{4'b}$), 143.3 ($C_{9'b}$), 144.5 ($C_{9'a}$), 150.2 ($C_{2'}$), 150.6 (C_4), 160.2 (C_2), 164.6 (CO); MS m/z 526 (M^+), 346, 181. Anal. Found: C, 81.60; H, 9.22%. Calcd for $C_{36}H_{46}O_3$: C, 82.08; H, 8.80%.

2-Fluorenyl 2-Hydroxy-4-pentadecylbenzoate (2). IR 3190 (OH), 1690 cm^{-1} (CO); ^{1}H NMR δ 0.88, 1.20–1.40, 1.65, 2.64, 3.95, 6.81, 6.87, 7.20, 7.32, 7.39, 7.40, 7.56, 7.79, 7.83, 8.00,

10.49 (OH); MS m/z 512 (M^+), 331. Anal. Found: C, 81.85; H, 8.60%. Calcd for $C_{35}H_{44}O_3$: C, 81.99; H, 8.65%.

2-Fluorenyl 4-Pentadecylbenzoate (3). IR 1730 cm^{-1} (CO); ^1H NMR δ 0.88, 1.20–1.40, 1.66, 2.70, 3.93, 7.21, 7.30, 7.33, 7.39, 7.40, 7.55, 7.78, 7.81, 8.14; MS m/z 496 (M^+), 315. Anal. Found: C, 84.89; H, 8.99%. Calcd for $C_{35}H_{44}O_2$: C, 84.63; H, 8.93%.

2-Fluorenyl 4-*n*-Butylbenzoate (4).[3] Mp 135–137 °C; IR 1730 cm^{-1} (CO); ^1H NMR δ 0.95, 1.38, 1.65, 2.72, 3.93, 7.21, 7.30, 7.33, 7.39, 7.40, 7.55, 7.78, 7.81, 8.14; MS m/z 342 (M^+), 181, 161. Anal. Found: C, 84.14; H, 6.43%. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47%.

2-Fluorenyl 4-*s*-Butylbenzoate (5). Mp 106–108 °C; IR 1730 cm^{-1} (CO); ^1H NMR δ 0.85, 1.29, 1.66, 2.72, 3.94, 7.21, 7.30, 7.34, 7.39, 7.40, 7.55, 7.78, 7.81, 8.16; MS m/z 342 (M^+), 181, 161. Anal. Found: C, 84.20; H, 6.50%. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47%.

7-Cyano-2-fluorenyl 2-Methoxy-4-pentadecylbenzoate (6). IR 2220 (CN), 1730 cm^{-1} (CO); ^1H NMR δ 0.88, 1.20–1.40, 1.66, 2.68, 3.96, 3.98, 6.86, 6.89, 7.28, 7.47, 7.69, 7.81–7.87, 7.99; MS m/z 551 (M^+), 345. Anal. Found: C, 80.77; H, 8.19; N, 2.67%. Calcd for $C_{37}H_{45}NO_3$: C, 80.54; H, 8.22; N, 2.54%.

7-Cyano-2-fluorenyl 2-Hydroxy-4-pentadecylbenzoate (7). IR 3220 (OH), 2220 (CN), 1680 cm^{-1} (CO); ^1H NMR δ 0.88 (3H, t, $J = 6.6$ Hz, Me), 1.20–1.40 (24H, m), 1.65 (2H, q, $J =$ 7.5 Hz), 2.64 (2H, t, $J = 7.5$ Hz), 4.00 (2H, s, $H_{9'}$), 6.82 (1H, dd, $J = 8.1$, 1.5 Hz, H_5), 6.87 (1H, d, J =1.5 Hz, H_3), 7.27 (1H, dd, $J = 8.4$, 1.5 Hz, $H_{3'}$), 7.45 (1H, d, $J = 1.5$ Hz, $H_{1'}$), 7.70 (1H, dd, $J = 8.1$, 1.5 Hz, $H_{6'}$), 7.83 (1H, d, $J = 1.5$ Hz, $H_{8'}$), 7.85 (1H, d, $J = 8.1$ Hz, $H_{5'}$), 7.88 (1H, d, $J = 8.4$ Hz, $H_{4'}$), 7.99 (1H, d, $J = 8.1$ Hz, H_6), 10.39 (1H, s, OH); ^{13}C NMR δ 14.1, 22.7, 29.2, 29.4, 29.4, 29.5, 29.7, 30.7, 31.9, 36.2, 36.8 ($C_{9'}$), 109.2 (C_1), 109.8 (CN), 117.3 (C_3), 119.0 ($C_{1'}$), 119.5 ($C_{7'}$), 120.3 (C_5), 120.4 ($C_{5'}$), 121.1 ($C_{3'}$), 121.8 ($C_{4'}$), 128.6 ($C_{8'}$), 130.1 (C_6), 131.4 ($C_{6'}$), 138.1 ($C_{4'a}$), 143.6 ($C_{9'b}$), 145.2 ($C_{4'b}$), 145.4 ($C_{9'a}$), 150.5 ($C_{2'}$), 153.3 (C_4), 162.3 (C_2), 169.0 (CO); MS m/z 537 (M^+), 331, 207. Anal. Found: C, 80.35; H, 7.99; N, 2.72%. Calcd for $C_{36}H_{43}NO_3$: C, 80.41; H, 8.06; N, 2.60%.

7-Cyano-2-fluorenyl 4-Pentadecylbenzoate (8). IR 2230 (CN), 1740 cm^{-1} (CO); ^1H NMR δ 0.88, 1.20–1.40, 1.66, 2.71, 3.99, 7.28, 7.34, 7.46, 7.69, 7.81–7.89, 8.13; MS m/z 521 (M^+), 315, 207. Anal. Found: C, 82.88; H, 8.35; N, 2.69%. Calcd for $C_{36}H_{43}NO_2$: C, 82.87; H, 8.31; N, 2.68%.

7-Cyano-2-fluorenyl 4-*n*-Butylbenzoate (9). IR 2230 (CN), 1740 cm^{-1} (CO); ^1H NMR δ 0.95, 1.39, 1.66, 2.72, 3.93, 7.27, 7.34, 7.46, 7.68, 7.80–7.88, 8.13; MS m/z 367 (M^+), 206, 161. Anal. Found: C, 81.61; H, 5.51; N, 3.80%. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81%.

7-Cyano-2-fluorenyl 4-*s*-Butylbenzoate (10). IR 2230 (CN), 1740 cm^{-1} (CO); ^1H NMR δ 0.85, 1.29, 1.67, 2.72, 3.99, 7.28, 7.34, 7.46, 7.69, 7.81–7.88, 8.13; MS m/z 367 (M^+), 206, 161. Anal. Found: C, 81.57; H, 5.59; N, 3.82%. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81%.

Biphenyl-4-yl 2-Methoxy-4-pentadecylbenzoate (11). Mp 58–59 °C; IR 1740 cm^{-1} (CO); ^1H NMR δ 0.88, 1.20–1.40, 1.66, 2.67, 3.95, 6.85, 6.88, 7.29, 7.35, 7.44, 7.57–7.63, 7.98; MS m/z 514 (M^+), 345. Anal. Found: C, 81.59; H, 9.13%. Calcd for $C_{35}H_{46}O_3$: C, 81.67; H, 9.01%.

Biphenyl-4-yl 2-Hydroxy-4-pentadecylbenzoate (12). Mp 78–79 °C; IR 3220 (OH), 1680 cm^{-1} (CO); ^1H NMR δ 0.88 (3H, t, $J = 6.6$ Hz, Me), 1.20–1.40 (24H, m), 1.64 (2H, q, $J =$ 7.5 Hz), 2.67 (2H, t, $J = 7.5$ Hz), 6.81 (1H, dd, $J = 8.4$, 1.8 Hz, H_5), 6.87 (1H, s, H_3), 7.28 (2H, d, $J = 8.4$ Hz, $H_{3',5'}$), 7.37 (1H, t, $J = 7.2$ Hz, $H_{4''}$), 7.46 (2H, t, $J = 7.2$, Hz, $H_{3'',5''}$), 7.60 (2H, d, $J = 7.2$ Hz, $H_{2'',6''}$), 7.64 (2H, d, $J = 8.4$ Hz, $H_{2',6'}$), 7.98 (1H, d, $J = 8.4$ Hz, H_6), 10.46 (1H, s, OH); ^{13}C NMR δ 14.1, 22.7, 29.2, 29.4, 29.5, 29.6, 29.7, 29.7, 30.7, 31.9, 36.2, 109.3 (C_1), 117.3 (C_3), 120.2 (C_5), 122.0 ($C_{3',5'}$), 127.2 ($C_{2'',6''}$), 127.5 ($C_{4''}$), 128.3 ($C_{2',6'}$), 128.8 ($C_{3'',5''}$), 130.2 (C_6), 139.5 ($C_{1'}$), 140.2 ($C_{1''}$), 149.5 ($C_{4'}$), 153.1 (C_4), 162.3 (C_2), 169.0 (CO); MS m/z 500 (M^+), 331. Anal. Found: C, 81.81; H, 8.89%. Calcd for $C_{34}H_{44}O_3$: C, 81.56; H, 8.86%.

Biphenyl-4-yl 4-Pentadecylbenzoate (13). Mp 95–97 °C; IR 1730 cm^{-1} (CO); ^1H NMR δ 0.88, 1.20–1.40, 1.66, 2.67, 7.28, 7.33, 7.36, 7.45, 7.60, 7.64, 8.13; MS m/z 484 (M^+), 315. Anal. Found: C, 84.49; H, 9.36%. Calcd for $C_{34}H_{44}O_2$: C, 84.25; H, 9.15%.

4′-Cyanobiphenyl-4-yl 2-Methoxy-4-pentadecylbenzoate (14). IR 2230 (CN), 1740 cm^{-1} (CO); ^1H NMR δ 0.88 (3H, t, $J = 6.6$ Hz, Me), 1.20–1.40 (24H, m), 1.66 (2H, q, $J = 7.2$ Hz), 2.68 (2H, t, $J = 7.8$ Hz), 3.95 (3H, s, OMe), 6.86 (1H, s, H_3), 6.89 (1H, d, $J = 7.8$ Hz, H_5), 7.33 (2H, d, $J = 8.4$ Hz, $H_{3',5'}$), 7.63 (2H, d, $J = 8.4$ Hz, $H_{2',6'}$), 7.66–7.75 (4H, m, $H_{2'',3'',5'',6''}$), 7.99 (1H, d, $J = 7.8$ Hz, H_6); ^{13}C NMR δ 14.1, 22.7, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.1, 31.9, 36.4, 56.0 (OMe), 110.9 ($C_{4''}$), 112.3 (C_3), 115.7 (C_1), 118.9 (CN), 120.4 (C_5), 122.7 ($C_{3',5'}$), 127.7 ($C_{2'',6''}$), 128.2 ($C_{2',6'}$), 132.4 (C_6), 132.6 ($C_{3'',5''}$), 136.5 ($C_{1'}$), 144.9 ($C_{1''}$), 151.0 (C_4), 151.5 ($C_{4'}$), 160.3 (C_2), 164.0 (CO); MS m/z 345. Anal. Found: C, 80.22; H, 8.34; N, 2.70%. Calcd for $C_{36}H_{45}NO_3$: C, 80.11; H, 8.40; N, 2.60%.

4′-Cyanobiphenyl-4-yl 2-Hydroxy-4-pentadecylbenzoate (15). IR 3300 (OH), 2220 (CN), 1690 cm^{-1} (CO); ^1H NMR δ 0.88, 1.20–1.40, 1.64, 2.64, 6.82, 6.87, 7.33, 7.66, 7.68–7.77, 7.98, 10.39; MS m/z 525 (M^+), 331. Anal. Found: C, 79.80; H, 8.19; N, 2.75%. Calcd for $C_{35}H_{43}NO_3$: C, 79.96; H, 8.26; N, 2.66%.

4′-Cyanobiphenyl-4-yl 4-Pentadecylbenzoate (16). IR 2220 (CN), 1740 cm^{-1} (CO); ^1H NMR δ 0.88, 1.20–1.40, 1.66, 2.71, 7.31–7.35, 7.64, 7.66–7.76, 8.13; MS m/z 509 (M^+), 315. Anal. Found: C, 82.39; H, 8.41; N, 2.89%. Calcd for $C_{35}H_{43}NO_2$: C, 82.47; H, 8.50; N, 2.75%.

4′-Cyanobiphenyl-4-yl 4-*n*-Butylbenzoate (17). IR 2230 (CN), 1740 cm^{-1} (CO); ^1H NMR δ 0.95, 1.38, 1.65, 2.72, 7.31–7.36, 7.64, 7.67–7.76, 8.14; MS m/z 355 (M^+), 161. Anal. Found: C, 80.76; H, 5.91; N, 4.07%. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94%.

4′-Cyanobiphenyl-4-yl 4-*s*-Butylbenzoate (18). IR 2230 (CN), 1730 cm^{-1} (CO); ^1H NMR δ 0.85, 1.28, 1.65, 2.72, 7.31–7.36, 7.64, 7.67–7.76, 8.15; MS m/z 355 (M^+), 161. Anal. Found: C, 80.89; H, 5.90; N, 4.07%. Calcd for $C_{24}H_{21}NO_2$: C, 81.10; H, 5.96; N, 3.94%.

References

1 W. Kast, "Landolt-Börnstein," 6th ed, Springer-Verlag, Berlin (1960), Vol. II, Part 2a, p. 266.

2 G. W. Gray, "The Molecular Physics of Liquid Crystals," ed by G. R. Luckhurst and G. W. Gray, Academic Press, New York, NY (1979), Chaps. 1 and 2.

3 S. L. Arora, B. Ziemnicka, and J. W. Doane, *Mol. Cryst. Liq. Cryst.*, **127**, 341 (1985).

4 Y. Takabayashi, T. Fukami, A. Yamamoto, T. Kimura, and M. Minabe, *Bull. Chem. Soc. Jpn.*, **73**, 1697 (2000).

5 F. H. Boardman, D. A. Dummur, M. C. Grossel, and G. R.

Luckhurst, *Chem. Lett.*, **2002**, 60.

6 Y. Takabayashi, T. Yusa, M. Minabe, T. Kimura, and M. Tsubota, *Bull. Chem. Soc. Jpn.*, **72**, 2755 (1999).

7 T. Sekine, Y. Takanishi, T. Niori, J. Watanabe, and H. Takezoe, *Jpn. J. Appl. Phys.*, **36**, L1201 (1997).

8 S. Shen, S. Diele, I. Wirt, and C. Tschierske, *J. Chem. Soc., Chem. Commun.*, **1988**, 2573.

9 "Ekishou Bin Ran," ed by editorial board of Ekishou Bin Ran, Maruzen, Tokyo, Japan (2000), p. 269.

10 W. F. Symes and C. R. Dawson, *Nature*, **171**, 841 (1953).

11 M. Saminathan and C. K. S. Pillai, *Polymer*, **41**, 3103 (2000).

12 C. Neil and H. M. Naim, *Proc.-R. Soc. Edinburgh, Sect. A*, **68**, 127 (1969).

13 I. R. Davison and D. M. Hall, *Mol. Cryst. Liq. Cryst.*, **129**, 17 (1985).

14 P. M. Downey and R. O. Zerbe, U. S. Patent 2670382 (Feb. 23, 1954); *Chem. Abstr.*, **49**, 4020 (1955).

15 P. G. Gassman, D. W. Macomber, and S. M. Willging, *J. Am. Chem. Soc.*, **107**, 2380 (1985).

16 W. H. de Jeu and J. van der Veen, *Mol. Cryst. Liq. Cryst.*, **40**, 1 (1977).

17 C.-J. Hsieh and G.-H. Hsiue, *Liq. Cryst.*, **16**, 469 (1994).

18 T. Sierra, J. L. Serrano, M. B. Ros, A. Ezcurra, and J. Zubia, *J. Am. Chem. Soc.*, **114**, 7645 (1992).

19 G. W. Gray and B. M. Worrall, *J. Chem. Soc.*, **1959**, 1545.

20 S. Takenaka, Y. Masuda, M. Iwano, H. Morita, S. Kusabayashi, H. Sugiura, and T. Ikemoto, *Mol. Cryst. Liq. Cryst.*, **168**, 111 (1989).