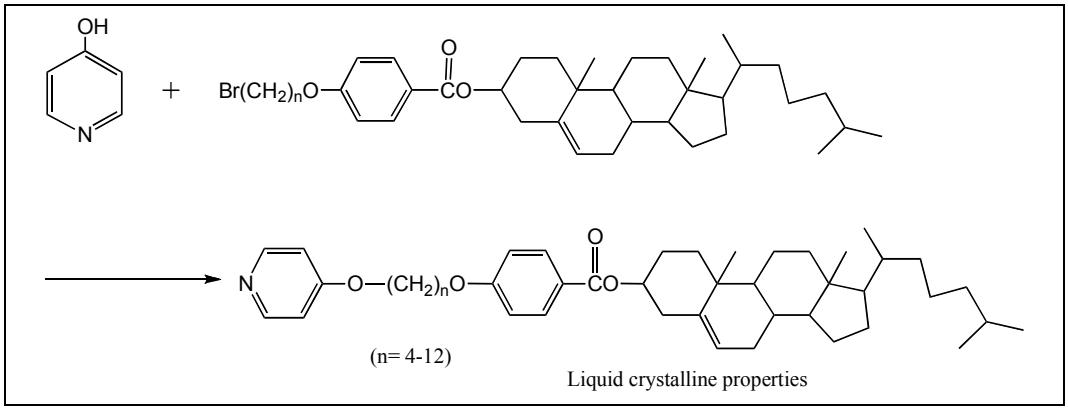
Synthesis and Liquid Crystalline Properties of Novel Pyridine Derivatives

Toshio Itahara

Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890-0065, Japan.
Email: itahara@be.kagoshima-u.ac.jp

Received February 19, 2007



The treatment of 4-hydroxypyridine with cholestery *p*-(ω-bromoalkyloxy)benzoates in *N,N*-dimethylformamide containing K_2CO_3 gave cholestery *p*-[ω-(4-pyridyloxy)alkyloxy]benzoates, which exhibited liquid crystalline properties

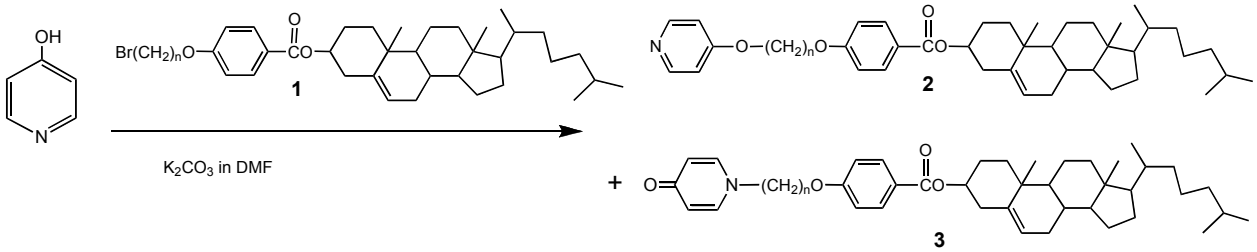
J. Heterocyclic Chem., **45**, 913 (2008).

INTRODUCTION

The hydrogen-bonded supramolecular liquid crystals containing pyridine derivatives have been extensively studied since the pioneering work of Kato and Frechet [1] and Lehn *et al* [2]. Although various liquid crystalline compounds with pyridine ring have been prepared, little attention has been paid to alkylation of 4-hydroxypyridine as a method for a preparation of liquid crystalline pyridine derivatives. The alkylation of 4-hydroxypyridine results in the alkylation of the phenolic oxygen of 4-hydroxypyridine or the nitrogen of 4-pyridone, but the details of the reaction are still unclear [3-9]. Furthermore, increasing interest is being shown in the tautomeric equilibrium between 4-hydroxypyridine and 4-pyridone in connection with the physiological action of pyridine and pyrimidine derivatives, *e.g.* pyrimidine nucleic acid bases [10-14]. On the other hand, cholestery benzoate is the first liquid crystalline compound [15], and in this connection, we have studied the reaction of nucleic acid bases with cholestery *p*-(ω-bromoalkyloxy)benzoates **(1)** [16,17]. The present paper reports a synthesis of new liquid crystalline compounds with pyridine ring by a treatment of 4-hydroxypyridine with **1**.

RESULTS AND DISCUSSION

The reaction of 4-hydroxypyridine with **1** in *N,N*-dimethylformamide (DMF) in the presence of K_2CO_3 gave the compounds **(2)** as main products and the compounds **(3)** as minor products. Although the ^{1}H-NMR data of **2** and **3** were similar, the aromatic regions were clearly different. The aromatic absorptions of **2** at δ 8.4 (d, 2H, J=6.0Hz) and δ 6.8 (d, 2H, J=6.0Hz) were assigned to the hydrogens of 4-substituted pyridine, while the aromatic absorptions of **3** were found at δ 7.3 (d, 2H, J=7.6Hz) and δ 6.4 (d, 2H, J=7.6Hz). Furthermore, the absorptions of **2** at δ 4.0 (t, 4H, J=6.0Hz) were assigned to the two CH_2-O parts, while the absorptions of **3** at δ 4.0 (t,



a: n = 4, **b**: n = 5, **c**: n = 6, **d**: n = 7, **e**: b = 8, **f**: n = 9, **g**: n = 10, **h**: n = 11, **i**: n = 12

Figure 1

2H, J=6.0Hz) and δ 3.75 (t, 2H, J=7.0Hz) were assigned to one CH_2-O part and one CH_2-N part, respectively.

The IR spectral data provided further evidence for the structures of **2** and **3**. The IR spectra of **2a** and **3a** are illustrated in Figure 2. The IR spectra of **2a-i** showed one C=O stretching band at 1703 cm^{-1}. On the other hand, two C=O stretching bands were found at 1703 and 1639 cm^{-1} for **3a-i**. On the basis of these ^{1}H-NMR and IR spectral data, it can be concluded that **2** and **3** are 4-alkyloxypyridines and N-alkyl substituted 4-pyridones, respectively. The structures of **2** and **3** are shown in Figure 1. The yields of **2** and **3** are summarized in Table 1. It can be seen from Table 1 that the ratio of the isolated yields of **2** and **3** is about 10:1. Therefore, the alkylation of 4-hydroxypyridine may be effective for the introduction of pyridine ring into liquid crystalline molecules.

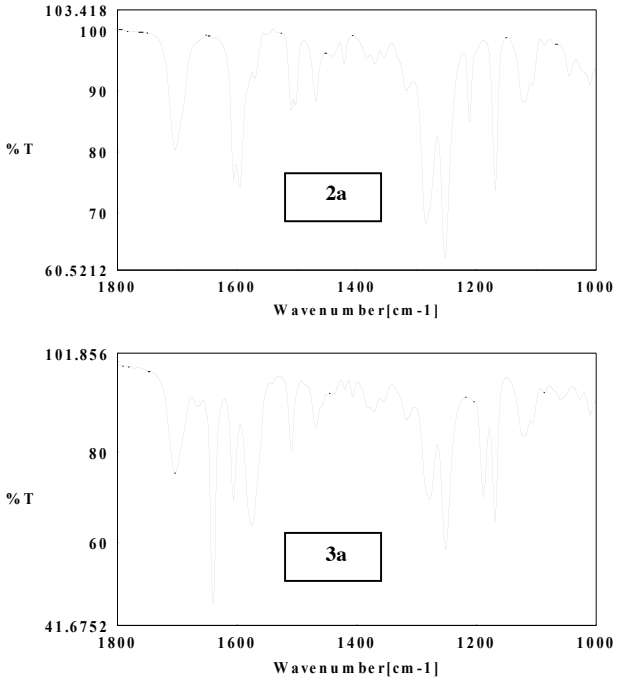


Figure 2. IR spectra of **2a** and **3a** in $CDCl_3$.

Table 1

The reaction of 4-hydroxypyridine with **1**

n	Products / Isolated yield (%)
4	**2a**/44, **3a**/4, **1a**/12
5	**2b**/46, **3b**/5, **1b**/15
6	**2c**/46, **3c**/5, **1c**/15
7	**2d**/41, **3d**/5, **1d**/12
8	**2e**/44, **3e**/5, **1e**/13
9	**2f**/ 42, **3f**/5, **1f**/13
10	**2g**/42, **3g**/4, **1g**/14
11	**2h**/40, **3h**/4, **1h**/11
12	**2i**/ 42, **3i**/4, **1i**/12

The thermal mesomorphic phases of **2a-i** were analyzed by using the differential scanning calorimeter (DSC) and the polarizing microscope. The polarizing microscopy observation substantiated the cholesteric liquid crystallinity of **2a-i**. Figure 3 shows the polarizing microscopic image of cholesteric liquid crystal of **2a** at 183 °C upon heating. The thermodynamic data of **2a-i** are summarized in Table 2. The relationship between the mesomorphic ranges of **2** and the length of the alkyl chain is shown in Figure 4. In spite of a clear odd-even effect of the melting points of **2a-i**, the transition temperature from liquid crystal to isotropic liquid did not show a similar odd-even effect.

Figure 3. The polarizing microscopic image of cholesteric liquid crystal of **2a** at 183 °C upon heating.

Table 2

Thermal behavior of **2**

Compd.	n	°C (ΔH: kJ/mol) *		
2a	4	C 153 (30.4)	N* 214 (0.7)	I
2b	5	C 130 (26.5)	N* 205 (0.7)	I
2c	6	C 148 (30.8)	N* 197 (0.8)	I
2d	7	C 114 (25.3)	N* 190 (0.8)	I
2e	8	C 126 (31.8)	N* 188 (0.9)	I
2f	9	C 93 (26.4)	N* 178 (0.8)	I
2g	10	C 110 (32.5)	N* 174 (1.0)	I
2h	11	C 90 (25.1)	N* 170 (0.9)	I
2i	12	C 111 (35.4)	N* 167 (0.9)	I

* The thermal mesomorphic ranges were determined by DSC upon heating at a rate of 5 °C. C: Crystal. N*: Cholesteric liquid crystal. I: Isotropic liquid.

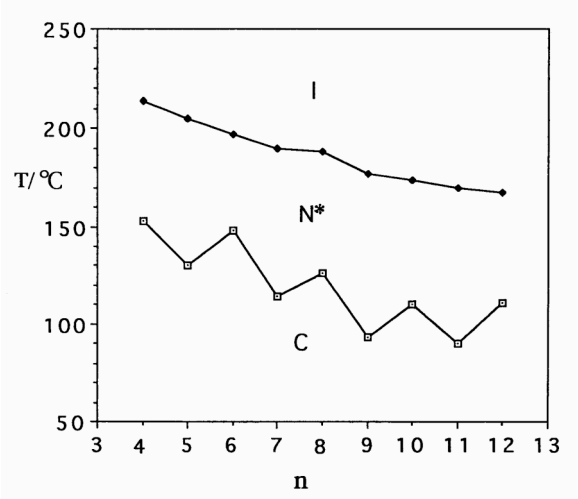


Figure 4. The relationship between the mesomorphic ranges of **2** and the carbon numbers (n) of the alkyl chain.

EXPERIMENTAL

The elemental analyses were performed in the Analytical Center of Kyoto University. The ^{1}H-NMR spectra (400 MHz) were obtained with a JEOL GSX 400 spectrometer. The chemical shifts (δ-values) were measured in parts per million (ppm) down-field from tetramethylsilane as an internal reference. The IR spectra were recorded with a JASCO FT/IR-420 spectrometer. The measurements in $CDCl_3$ were made with a 0.1 mm KBr cell. Differential scanning calorimetry (DSC) measurements were carried out with a Shimadzu DSC-60. Microscopy observations were performed under a Nikon Eclipse E600 POL equipped with a hot stage (Linkam LK-600PH). Cholestery *p*-(ω-bromoalkyloxy)benzoates **(1)** were prepared by the reaction of cholesteryl *p*-hydroxybenzoate [18] and α,ω-dibromoalkane according to the procedure described before [16,17].

Reaction of 4-hydroxypyridine with cholestery *p*-(ω-bromoalkyloxy)benzoates (1). A solution of 4-hydroxypyridine (0.5 mmol) and **1** (0.5 mmol) in DMF (50 ml) containing K_2CO_3 (0.5 mmol) was stirred at room temperature for 24 h under nitrogen atmosphere. The reaction mixture was evaporated to give a residue, which was chromatographed on silica gel. By monitoring at 254 nm, elution by chloroform gave **2** together with a small amount of **3**.

Cholestery *p*-[(4-(4-pyridyloxy)butoxy)benzoate (2a). ^{1}H-NMR ($CDCl_3$) δ 8.42(d, 2H, Pyridine, J=6.0Hz), 7.99(d, 2H, Ph, J=8.8Hz), 6.90(d, 2H, Ph, J=8.8Hz), 6.80(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.83(m, Chol-3, 1H), 4.09(broad t, 4H, J=6.0 Hz), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 26H). IR ($CDCl_3$) 2951, 2870, 1703, 1606, 1595, 1510, 1470, 1421, 1369, 1317, 1284, 1252, 1211, 1169, 1122 cm^{-1}. *Anal*. Calcd for $C_{43}H_{61}NO_4$: C: 78,74; H:9.37; N:2.14%. Found: C:78.75; H:9.47; N:2.08%.

Cholestery *p*-[(5-(4-pyridyloxy)pentyloxy)benzoate (2b). ^{1}H-NMR ($CDCl_3$) δ8.41(d, 2H, Pyridine, J=6.0Hz), 7.99(d, 2H, Ph, J=8.8Hz), 6.90(d, 2H, Ph, J=8.8Hz), 6.79(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.04(t, 4H, J=6.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 28H). IR ($CDCl_3$) 2949, 2870, 1703, 1606, 1597, 1508, 1470, 1421, 1371, 1317, 1284, 1254, 1211, 1169, 1122 cm^{-1}. *Anal*. Calcd for $C_{44}H_{63}NO_4$: C: 78.88; H:9.48; N:2.09%. Found: C:79.10; H:9.74; N:2.04%.

Cholestery *p*-[(6-(4-pyridyloxy)hexyloxy)benzoate (2c). ^{1}H-NMR ($CDCl_3$) δ8.41(d, 2H, Pyridine, J=6.0Hz), 7.99(d, 2H, Ph, J=8.8Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.79(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.02(t, 4H, J=6.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 30H). IR ($CDCl_3$) 2947, 2870, 1703, 1605, 1597, 1510, 1470, 1421, 1369, 1317, 1284, 1254, 1211, 1169, 1122 cm^{-1}. *Anal*. Calcd for $C_{45}H_{65}NO_4$: C: 79.02; H:9.58; N:2.05%. Found: C:78.89; H:9.79; N:2.03%.

Cholestery *p*-[(7-(4-pyridyloxy)heptyloxy)benzoate (2d). ^{1}H-NMR ($CDCl_3$) δ 8.41(d, 2H, Pyridine, J=6.0Hz), 7.98(d, 2H, Ph, J=8.8Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.79(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.01(t, 4H, J=6.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 32H). IR ($CDCl_3$) 2941, 2870, 1703, 1606, 1598, 1510, 1468, 1421, 1371, 1317, 1284, 1254, 1211, 1169, 1121 cm^{-1}. *Anal*. Calcd for $C_{46}H_{67}NO_4$: C: 79.15; H:9.67; N:2.01%. Found: C:79.48; H:9.97; N:1.97%.

Cholestery *p*-[(8-(4-pyridyloxy)octyloxy)benzoate (2e). ^{1}H-NMR ($CDCl_3$) δ 8.41(d, 2H, Pyridine, J=6.0Hz), 7.98(d, 2H, Ph, J=8.8Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.79(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 4H, J=6.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 34H). IR ($CDCl_3$) 2935, 2856, 1703, 1605, 1597, 1510, 1468, 1421, 1369, 1317, 1284, 1254, 1211, 1169, 1121 cm^{-1}. *Anal*. Calcd for $C_{47}H_{69}NO_4$: C: 79.28; H: 9.77; N:1.97%. Found: C;79.26; H:9.83; N:1.98%.

Cholestery *p*-[(9-(4-pyridyloxy)nonyloxy)benzoate (2f). ^{1}H-NMR ($CDCl_3$) δ8.41(d, 2H, Pyridine, J=6.0Hz), 7.98(d, 2H, Ph, J=8.8Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.79(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 4H, J=6.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 36H). IR ($CDCl_3$) 2941, 2868, 1703, 1605, 1597, 1510, 1468, 1421, 1371, 1317, 1284, 1254, 1211, 1169, 1119 cm^{-1}. *Anal*. Calcd for $C_{48}H_{71}NO_4 \cdot ½H_2O$: C: 78.42; H: 9.87; N:1.91%. Found: C: 78.12; H: 9.81 N: 1.90%.

Cholestery *p*-[(10-(4-pyridyloxy)decyloxy)benzoate (2g). ^{1}H-NMR ($CDCl_3$) δ 8.41(d, 2H, Pyridine, J=6.0Hz), 7.98(d, 2H, Ph, J=8.8Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.79(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 4H, J=6.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 38H). IR ($CDCl_3$) 2937, 2856, 1703, 1606, 1597, 1510, 1468, 1421, 1369, 1317, 1284, 1254, 1211, 1169, 1121 cm^{-1}. *Anal*. Calcd for $C_{49}H_{73}NO_4$: C: 79.52; H: 9.94; N: 1.89%. Found: C: 79.35; H: 10.06; N:1.84%.

Cholestery *p*-[(11-(4-pyridyloxy)undecyloxy)benzoate (2h). ^{1}H-NMR ($CDCl_3$) δ8.40(d, 2H, Pyridine, J=6.0Hz), 7.98(d, 2H, Ph, J=8.8Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.79(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 4H, J=6.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 40H). IR ($CDCl_3$) 2943, 2870, 1703, 1605, 1597, 1508, 1468, 1421, 1371, 1317, 1284, 1254, 1211, 1169, 1122 cm^{-1}. *Anal*. Calcd for $C_{50}H_{75}NO_4$: C: 79.63; H: 10.02; N: 1.86%. Found: C: 79.40; H: 10.13; N: 1.89%.

Cholestery *p*-[(12-(4-pyridyloxy)dodecyloxy)benzoate (2i). ^{1}H-NMR ($CDCl_3$) δ8.40(d, 2H, Pyridine, J=6.0Hz), 7.98(d, 2H, Ph, J=8.8Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.79(d, 2H, Pyridine, J=6.0Hz), 5.41(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 4H, J=6.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 42H). IR ($CDCl_3$) 2935, 2856, 1703, 1605, 1597, 1508, 1468, 1421, 1371, 1317, 1284, 1254, 1211, 1169, 1120 cm^{-1}. *Anal*. Calcd for $C_{51}H_{77}NO_4 \cdot ½H_2O$: C: 78.82; H: 10.12; N: 1.82%. Found: C: 78.75; H: 10.07; N: 1.80%.

Cholestery *p*-[4-(4-pyridon-1-yl)butoxy)benzoate (3a). ^{1}H-NMR ($CDCl_3$) δ8.00(d, 2H, Ph, J=8.8Hz), 7.30(d, 2H, Pyridone, J=7.6Hz), 6.88(d, 2H, Ph, J=8.8Hz), 6.41(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.83(m, Chol-3, 1H), 4.06(t, 2H, J=6.0 Hz), 3.87(t, 2H, J=7.0 Hz), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27,J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 26H). IR ($CDCl_3$) 2951, 2870, 1703, 1639, 1606, 1576, 1510, 1470, 1371, 1317, 1278, 1252, 1169, 1122 cm^{-1}.

Cholestery *p*-[5-(4-pyridon-1-yl)pentloxy)benzoate (3b). ^{1}H-NMR ($CDCl_3$) δ7.99(d, 2H, Ph, J=8.8Hz), 7.26(d, 2H, Pyridone, J=7.6Hz), 6.88(d, 2H, Ph, J=8.8Hz), 6.40(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.02(t, 2H, J=6.0HZ), 3.80(t, 2H, J=7.0HZ),2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 28H). IR ($CDCl_3$) 2949, 2870, 1703, 1639, 1606, 1576, 1510, 1468, 1371, 1317, 1279, 1252, 1169, 1122 cm^{-1}.

Cholestery *p*-[6-(4-pyridon-1-yl)hexyloxy)benzoate (3c). ^{1}H-NMR ($CDCl_3$) δ7.99(d, 2H, Ph, J=8.8Hz), 7.26(d, 2H, Pyridone, J=7.6Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.40(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 2H, J=6.0HZ), 3.77(t, 2H, J=7.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 30H). IR ($CDCl_3$) 2944, 2868, 1703, 1639, 1606, 1576, 1510, 1468, 1371, 1317, 1279, 1254, 1169, 1122 cm^{-1}.

Cholestery *p*-[7-(4-pyridon-1-yl)heptyloxy)benzoate (3d). ^{1}H-NMR ($CDCl_3$) δ7.98(d, 2H, Ph, J=8.8Hz), 7.26(d, 2H, Pyridone, J=7.6Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.40(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 2H, J=6.0HZ), 3.75(t, 2H, J=7.0HZ),2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 32H). IR ($CDCl_3$) 2944, 2868, 1703, 1639, 1606, 1576, 1510, 1468, 1371, 1317, 1279, 1254, 1169, 1122 cm^{-1}.

Cholestery *p*-[8-(4-pyridon-1-yl)oxtyloxy)benzoate (3e). ^{1}H-NMR ($CDCl_3$) δ7.98(d, 2H, Ph, J=8.8Hz), 7.26(d, 2H, Pyridone, J=7.6Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.40(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 2H, J=6.0HZ), 3.75(t, 2H, J=7.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 34H). IR ($CDCl_3$) 2937, 2868, 1703, 1639, 1606, 1576, 1510, 1468, 1369, 1317, 1279, 1254, 1169, 1121 cm^{-1}.

Cholestery *p*-[9-(4-pyridon-1-yl)nonyloxy)benzoate (3f). ^{1}H-NMR ($CDCl_3$) δ7.98(d, 2H, Ph, J=8.8Hz), 7.26(d, 2H, Pyridone, J=7.6Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.40(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 2H, J=6.0HZ), 3.75(t, 2H, J=7.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 36H). IR ($CDCl_3$) 2935, 2856, 1703, 1639, 1606, 1574, 1510, 1468, 1371, 1317, 1279, 1254 1169, 1122 cm^{-1}.

Cholestery *p*-[10-(4-pyridon-1-yl)decyloxy)benzoate (3g). ^{1}H-NMR ($CDCl_3$) δ7.98(d, 2H, Ph, J=8.8Hz), 7.26(d, 2H, Pyridone, J=7.6Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.40(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 2H, J=6.0HZ), 3.75(t, 2H, J=7.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 38H). IR ($CDCl_3$) 2931, 2856, 1703, 1639, 1606, 1576, 1510, 1468, 1371, 1315, 1277, 1254, 1169, 1119 cm^{-1}.

Cholestery *p*-[11-(4-pyridon-1-yl)undecyloxy)benzoate (3h). ^{1}H-NMR ($CDCl_3$) δ7.98(d, 2H, Ph, J=8.8Hz), 7.26(d, 2H, Pyridone, J=7.6Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.40(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 2H, J=6.0HZ), 3.75(t, 2H, J=7.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 40H). IR ($CDCl_3$) 2935, 2856, 1703, 1639, 1606, 1574, 1510, 1468, 1371, 1317, 1279, 1254 1169, 1122 cm^{-1}.

Cholestery *p*-[12-(4-pyridon-1-yl)dodecyloxy)benzoate (3i). ^{1}H-NMR ($CDCl_3$) δ7.98(d, 2H, Ph, J=8.8Hz), 7.26(d, 2H, Pyridone, J=7.6Hz), 6.89(d, 2H, Ph, J=8.8Hz), 6.40(d, 2H, Pyridone, J=7.6Hz), 5.42(d, 1H, Chol-6, J=3.6Hz), 4.82(m, Chol-3, 1H), 4.00(t, 2H, J=6.0HZ), 3.75(t, 2H, J=7.0HZ), 2.45(d, 2H, Chol-4, J=7.6Hz), 1.07 (s, 3H, Chol-19or18), 0.92 (d, 3H, Chol-21, J=6.4 Hz), 0.87 (dd, 6H, Chol-26,27, J=6.4, J=1.6 Hz), 0.69 (s, 3H, Chol-18or19), 2.10-0.90 (m, 42H). IR ($CDCl_3$) 2933, 2856, 1703, 1639, 1606, 1576, 1510, 1468, 1371, 1317, 1277, 1254, 1169, 1120 cm^{-1}.

Acknowledgement. The author thanks Mr. T. Yoshitake for his technical assistance.

REFERENCES

[1] Kato, T.; Frecht. M. J. *J. Am. Chem. Soc.*, **1989**, *111*, 8533.
[2] Fouquey, C.; Lehn, J-M.; Levelut, A-M. *Adv. Mater*., **1990**, *2*, 254.
[3] Adams, R.; Johnson, J. L. *J. Am, Chem, Soc*.,**1949**, *71*, 705.
[4] Hopkins, G. C.; Jonak, J. P.; Minnemeyer, H. J.; Tieckelmann, H. *J. Org. Chem.*, **1967**, *32*, 4040.
[5] Dou, H.; J-M, Hassanaly, P.; Metzger, J. *J. Heterocyc. Chem*., **1977**, *14*, 321.
[6] Guerry, P.; Neier, R. *Synthesis*, **1984**, 485.
[7] Vorbruggen, H.; Krolikewwicz, K. *Chem. Ber*., **1984**, *117*, 1523.
[8] Johnson, B. L.; Kitahara, Y.; Weakley, T. J. R.; Keana, J. F. W. *Tetrahedron Lett*., **1993**, *34*, 5555.
[9] You, F.; Twieg, R. J. *Tetrahedron Lett*., **1999**, *40*, 8759.
[10] Beak, P. *Acc. Chem. Res*., **1977**, *10*, 186.
[11] Beak, P.; Covington, J. B. *J. Am. Chem. Soc*., **1978**, *100*, 3961.
[12] Reimers, J. R.; Hall, L. E.; Hush, N. *J. Phys. Chem. A*, **2000**, *104*, 5087.
[13] Tsuchida, N.; Yamabe, S. *J. Phys. Chem. A*, **2005**, *109*, 1974.
[14] Sanchez, R.; Giuliano, B. M.; Melandri, S.; Caminati, W. *Chem. Phys. Lett*., **2006**, *425*, 6.
[15] Reinitzer, F. *Monatsh Chem*., **1888**, *9*, 421.
[16] Itahara, T.; Sunose, M.; Kameda, T.; Ueda, T. *Chem. Phys. Chem*. **2002**, 378.
[17] Itahara, T.; Yokogawa, Y. *J. Mol. Struct*., **2007**, *827*, 95.
[18] Evan, M.; Heinrich, B.; Guillon, D.; Guldi, D. M.; Prato, M.; Deschenaux, R. *Chem. Eur. J*. **2001**, *7*, 2595.