Synthesis of Schiff Base-type Liquid Crystalline Crown Ethers Containing Dibenzo-18-Crown-6 Unit

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The synthesis and characterization of novel Schiff base liquid crystalline crown ethers prepared from the intermediates 4-(4'-alkoxylbiphenyl-4-carbonyl)benzaldehyde, *cis*- and *trans*-4,4'-diaminodibenzo-18-crown-6 are described. The structure of these compounds have been well characterized by elemental analysis, IR, ¹H NMR and MS spectroscopy. The liquid-crystalline behavior of these compounds was also inverstigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) with a heating stage and polarimetric analysis.

Keywords Schiff base, liquid crystalline crown ether, thermotropic liquid crystal, phase transition

Introduction

Recently, much interest has been attracted to the new liquid crystalline materials in the field of chiral recoganization, ion transportation, function membranes, transferring signal and information at the molecular level.¹⁻³ Nematic, smectic, discotie and columnar mesomorphic crown ethers⁵⁻⁸ have been reported since cholesterol mesomorphic crown ethers were first reported by Bogatskaya *et al.*⁴ in 1982.

It is well known that liquid crystalline crown ether possesses the properties of both liquid crystal and crown ether. For example, by connecting crown ether ring to mesogenic units with the base bond, the recognizing part for the difference of coexisting metal ion can be formed. These can make them widely used because of their fine-order structure and functional group. To date, there is few reports on the study of Schiff base type liquid crystalline crown ethers.^{9,10} In this work, a series of novel Schiff base liquid crystalline crown ethers was designed and synthesized in order to investigate the relationship between the structure and their liquid crystalline properties.

Experimental

General

Melting points were measured on a WRS-1 melting point apparatus and the thermometer was uncorrected. Elemental analysis were performed with a Carlo Erba 1160 elemental analyzer. IR spectra were recorded on a Perking-Elmer 1750 FT-IR spectrophotometer with KBr pellets. ¹H NMR spectra were recorded on a Bruker

DPX 400 spectrometer using DMSO- d_6 or CDCl₃ or CF₃COOD as an internal standard. Mass spectra were recorded on a VG-ZAB-HS spectrometer in FAB and a Bruker inc. BiflexIII apparatus with MALDI-TOF technique, using CCA as matrix. This instrument was equipped with a nitrogen laser (337 nm, pulse length 3 ns). It was operated at an accelerating potential of 20 kV. Specific rotations were measured on a WZZ-1 automatic Polarimeter. Differential Scanning Calorimetry (DSC) was recorded on a NETZCH DSC-204 Calorimeter with a data system at a heating rate of 10 $^{\circ}$ C /min. The phase transition temperatures shown in this paper are values of peaks in the transition temperatures on DSC traces. A Nikon Ecliphse E600 polarizing microscope equipped with a hot state was used to observe various mesophases. Dichloromethane, petroleum ether, pyridine, triethylamine and thionyl chloride were got commercially, and purified according to a reported procedure.¹¹ Chemical reagents used were of A.R. grade or chemical grade without further purification.

The target compounds were synthesized according to the procedures as shown in Scheme 1.

4-Alkoxyltosylate (1), 4-alkoxybiphenyl-4'-carboxylic acid (2), 4-alkoxy biphenyl-4'-carbonyl-chloride (3), 4-(4'-alkoxybipnenyl-4-carboxy)-benzaldehyde (4), dibenzo-18-crown-6 (5), dinitrodibenzo-18-crown-6 (6I, 6II), and diaminodibenzo-18-crown-6 (7I, 7II) were prepared as described.^{12,13} The condensation of compounds 7I or 7II with compounds 4 gave the target compounds 8I and 8II, respectively. Then these target compounds were purified by recrystallization in a mixed solvent of CHCl₃/ethanol.

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Scheme 1 Synthetic procedure of the target compounds



4,4'-Bis[(4'-alkoxybiphenyl-4-carboxyl)benzylideneamino]dibenzo-18-crown-6 (8)

Taking **8IA** as an example: **4A** (1.800 g, 4.636 mmol) and ethanol (250 mL) were mixed at refluxing under N₂ and **7I** (0.9052 g, 2.3184 mmol) was added. The solution allowed refluxing for 6 h. Then, the solution was cooled, filtrated to give the product. The product was recrystallized in a mixed solvent of CHCl₃/ethanol (volume ration: 2/1) and dried in vacuum to give **8IA** as light yellow crystals (2.4980 g). The compounds **8IB**, **8IC**, **8ID** and **8II** were synthesized with similar procedure to that of the compound **8IA**. The data for compounds 8I-8 II were shown as follows:

8IA: Yield, 95.2%; $[\alpha]_D^{20} + 8.65$ (*c* 0.25, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ : 8.48 (s, 2H, 2×CH=N), 8.24 (d, J=8.4 Hz, 4H, ArH), 7.97 (d, J=8.8 Hz, 4H, ArH), 7.70 (d, J=8.8 Hz, 4H, ArH), 7.60 (d, J=8.8 Hz, 4H, ArH), 7.35 (d, J=8.4 Hz, 4H, ArH), 7.01 (d, J=8.8 Hz, 4H, ArH), 6.90—6.88 (m, 6H, 2×ArH₃), 4.24 (t, J=5.6 Hz, 12H, 6×ArOCH₂), 4.08—4.06 (m, 8H, 2×CH₂OCH₂), 1.62—1.57 (m, 2H, 2×C*H), 1.24—1.16 (m, 4H, 2×CH₂), 1.05 (d, J=6.4 Hz, 6H, 2 ×C*HCH₃), 0.97 (t, J=7.2 Hz, 6H, 2×CH₃); IR (KBr) *v*: 1729, 1602, 1580, 1508, 1262, 1129, 875, 823 cm⁻¹; MALDI-TOF MS m/z: 1131 (M⁺), 1154 [M+Na]⁺. Anal. calcd for C₇₀H₇₀N₂O₁₂: C 74.32, H 6.24, N 2.48; found C 74.37, H 6.20, N 2.41.

8IB: Yield, 92.3%; ¹H NMR (CDCl₃, 400 MHz) δ : 8.48 (s, 2H, 2×CH=N), 8.24 (d, J=8.0 Hz, 4H, ArH), 7.97 (d, J=8.4 Hz, 4H, ArH), 7.70 (d, J=8.4 Hz, 4H, ArH), 7.60 (d, J=8.8 Hz, 4H, ArH), 7.35 (d, J=8.0 Hz, 4H, ArH), 7.01 (d, J=8.8 Hz, 4H, ArH), 6.91—6.88 (m, 6H, 2×ArH₃), 4.24 (t, J=4.8 Hz, 12H, 6×ArOCH₂), 4.07—4.00 (m, 8H, 2×CH₂OCH₂), 1.84—1.30 [m, 24H, 2×(CH₂)₆], 0.90 (t, J=5.6 Hz, 6H, 2×CH₃); IR (KBr) *v*: 1732, 1602, 1580, 1510, 1265, 1130, 878, 825 cm⁻¹; MALDI-TOFMS *m*/*z*: 1216 [M+1]⁺, 1238 [M+Na]⁺. Anal. calcd for C₇₆H₈₂N₂O₁₂: C 75.10, H 6.80, N 2.30; found C 75.03, H 6.85, N 2.21.

8IC: Yield, 90.2%; ¹H NMR (CDCl₃, 400 MHz) δ : 8.49 (s, 2H, 2×CH=N), 8.24 (d, J=7.6 Hz, 4H, ArH), 7.99 (d, J=8.4 Hz, 4H, ArH), 7.71 (d, J=7.6 Hz, 4H, ArH), 7.60 (d, J=8.0 Hz, 4H, ArH), 7.44 (d, J=8.0 Hz, 4H, ArH), 7.35 (d, J=8.4 Hz, 4H, ArH), 7.01—6.82 (m, 6H, 2×ArH₃), 4.23 (t, J=4.8 Hz, 12H, 6×ArOCH₂), 4.07—4.00 (m, 8H, 2×CH₂OCH₂), 1.84—1.29 [m, 32H, 2×(CH₂)₈], 0.89 (t, J=5.6Hz, 6H, 2×CH₃); IR (KBr) *v*: 1730, 1602, 1580, 1510, 1264, 1130, 872, 821 cm⁻¹; MALDI-TOFMS *m*/*z*: 1271 (M⁺), 1294 [M+Na]⁺. Anal. calcd for C₈₀H₉₀N₂O₁₂: C 75.56, H 7.13, N 2.20; found C 75.61, H 7.10, N 2.09.

8ID: Yield, 90.2%; ¹H NMR (CDCl₃, 400 MHz) δ : 8.48 (s, 2H, 2×CH=N), 8.24 (d, J=8.4 Hz, 4H, ArH), 7.97 (d, J=8.8 Hz, 4H, ArH), 7.70 (d, J=8.4 Hz, 4H, ArH), 7.60 (d, J=8.8 Hz, 4H, ArH), 7.43 (d, J=8.4 Hz, 4H, ArH), 7.35 (d, J=8.8 Hz, 4H, ArH), 7.01—6.88 (m, 6H, 2×ArH₃), 4.23 (t, J=4.8 Hz, 12H, 6×ArOCH₂), 4.08—4.00 (m, 8H, 2×CH₂OCH₂), 1.84—1.27 [m, 40H, 2×(CH₂)₁₀], 0.89 (t, J=6.4 Hz, 6H, 2×CH₃); IR (KBr) *v*: 1731, 1602, 1580, 1509 , 1265, 1130, 878, 821 cm⁻¹; MALDI-TOFMS *m*/*z*: 1328 [M+1]⁺, 1350 [M+Na]⁺. Anal. calcd for C₈₄H₉₈N₂O₁₂: C 75.99, H 7.44, N 2.11; found C 75.92, H 7.47, N 2.01.

8IIA: Yield, 94.2%; $[α]_D^{20}$ +8.60 (*c* 0.25, CHCl₃); ¹H NMR (CDCl₃, 400 MHz) δ: 8.49 (s, 2H, 2×CH=N), 8.25 (d, *J*=8.4 Hz, 4H, ArH), 7.97 (d, *J*=8.8 Hz, 4H, ArH), 7.71 (d, *J*=8.8 Hz, 4H, ArH), 7.60 (d, *J*=8.8 Hz, 4H, ArH), 7.71 (d, *J*=8.8 Hz, 4H, ArH), 7.60 (d, *J*=8.8 Hz, 4H, ArH), 7.01 (d, *J*=8.8 Hz, 4H, ArH), 7.36 (d, *J*=8.8 Hz, 4H, ArH), 7.01 (d, *J*=8.8 Hz, 4H, ArH), 6.90—6.88 (m, 6H, 2×ArH₃), 4.24 (t, *J*=5.6 Hz, 12H, 6×ArOCH₂), 4.08—4.06 (m, 8H, 2×CH₂OCH₂), 1.62—1.55 (m, 2H, 2×C*H), 1.24—1.16 (m, 4H, 2×CH₂), 1.05 (d, *J*=6.8 Hz, 6H, 2×C*HCH₃), 0.97 (t, *J*=7.2 Hz, 6H, 2×CH₃); IR (KBr) *v*: 1730, 1604, 1580, 1510, 1260, 1136, 875, 824 cm⁻¹; MALDI-TOFMS *m*/*z*: 1131 (M⁺), 1154 [M+Na]⁺. Anal. calcd for C₇₀H₇₀N₂O₁₂: C 74.32, H 6.24, N 2.48; found C 74.36, H 6.29, N 2.57.

8IIB: Yield, 93.4%; ¹H NMR (CDCl₃, 400 MHz) δ : 8.49 (s, 2H, 2×CH=N), 8.25 (d, J=8.4 Hz, 4H, ArH), 7.97 (d, J=8.4 Hz, 4H, ArH), 7.71 (d, J=8.8 Hz, 4H, ArH), 7.60 (d, J=8.8 Hz, 4H, ArH), 7.36 (d, J=8.8 Hz, 4H, ArH), 7.01 (d, J=8.4 Hz, 4H, ArH), 6.90–6.883 (m, 6H, 2×ArH₃), 4.24 (t, J=4.8 Hz, 12H, 6× ArOCH₂), 4.08—4.01 (m, 8H, 2×CH₂OCH₂), 1.84— 1.30 [m, 24H, 2×(CH₂)₆], 0.90 (t, J=6.4 Hz, 6H, 2× CH₃); IR (KBr) v: 1730, 1602, 1580, 1510, 1260, 1132, 875, 824 cm⁻¹; MALDI-TOFMS m/z: 1216 [M+1]⁺, 1238 [M+Na]⁺. Anal. calcd for C₇₆H₈₂N₂O₁₂: C 75.10, H 6.80, N2.30; found C 75.05, H 6.76, N 2.39.

8IIC: Yield, 93.3%; ¹H NMR (CDCl₃, 400 MHz) δ : 8.49 (s, 2H, 2×CH=N), 8.25 (d, *J*=8.0 Hz, 4H, ArH), 7.97 (d, *J*=8.4 Hz, 4H, ArH), 7.70 (d, *J*=8.8 Hz, 4H, ArH), 7.60 (d, *J*=8.8 Hz, 4H, ArH), 7.36 (d, *J*=8.0 Hz, 4H, ArH), 7.01 (d, *J*=8.4 Hz, 4H, ArH), 6.90—6.82 (m, 6H, 2×ArH₃), 4.25 (t, *J*=4.8 Hz, 12H, 6×ArOCH₂), 4.07—4.00 (m, 8H, 2×CH₂OCH₂), 1.84—1.27 [m, 32H, 2×(CH₂)₈], 0.90 (t, *J*=6.4 Hz, 6H, 2×CH₃); IR (KBr) *v*: 1730, 1602, 1580, 1509, 1260, 1135, 877, 824 cm⁻¹; MALDI-TOF MS *m*/*z*: 1271 (M⁺), 1294 [M+Na]⁺. Anal. calcd for C₈₀H₉₀N₂O₁₂: C 75.56, H 7.13, N 2.20; found C 75.50, H 7.17, N 2.10.

8IID: Yield, 92.7%; ¹H NMR (CDCl₃, 400 MHz) δ : 8.49 (s, 2H, 2×CH=N), 8.25 (d, J=8.4Hz, 4H, ArH), 7.97 (d, J=8.4 Hz, 4H, ArH), 7.71 (d, J=8.8 Hz, 4H, ArH), 7.60 (d, J=8.8 Hz, 4H, ArH), 7.35 (d, J=8.8 Hz, 4H, ArH), 7.01 (d, J=8.4 Hz, 4H, ArH), 6.90—6.88 (m, 6H, 2×ArH₃), 4.24 (t, J=4.8 Hz, 12H, 6×ArOCH₂), 4.06—4.01 (m, 8H, 2×CH₂OCH₂), 1.84—1.28 [m, 40H, 2×(CH₂)₁₀], 0.89 (t, J=6.4 Hz, 6H, 2×CH₃); IR (KBr) *v*: 1730, 1602, 1580, 1509, 1260, 1130, 878, 824 cm⁻¹; MALDI-TOF MS *m*/*z*: 1328 [M+1]⁺, 1350 [M+Na]⁺. Anal. calcd for C₈₄H₉₈N₂O₁₂: C 75.99, H 7.44, N 2.11; found C 75.95, H 7.41, N 2.19.

Results and discussion

Optical activity of the chiral compounds

The optical activity was measured with a dilute solution (*ca.* 10^{-2} g/mL) of sample on a WZZ-1 automatic polarimeter at 20 °C with a beam of 589.44 nm. The length of the sample cell used was 200 nm. As shown in the Table 1, all the chiral materials prepared from (*S*)-(-)-2-methyl-1-butanol which has a specific optical rotation of -6.3° are optically active. Care must be taken to protect the chiral center by first activating the alcohol into its tosylate and by using mild reaction conditions during measuring. The result obtained for 4-[(*S*)-2-methylbutoxyl]biphehyl-4'-carboxylic acid showed a specific optical rotation of 12.87° (deg · dm⁻¹ · g⁻¹ · cm³). Although these chiral compounds showed significant optical activities, no optical purity was determined for them.¹⁴

Study and characterization of the chemical structure and liquid crystalline phase

The chemical structures of **2**, **4**, **5**, **6**, **7** and **8** were determined by elemental analysis, IR, ¹H NMR and MS spectroscopy. The phase transition temperatures of **8I** and **8II** were measured by DSC and POM and the type of mesophase was determined by observing the meso-

Compd	Phase transition temperature/°C (corresponding en- thalpy changes, $\mathbf{J} \cdot \mathbf{g}^{-1}$)	Phase length of mesomorphic			L/D
		S/°C	Ch/°C	N/°C	
8IA	C220.7(6.72)Sc*257.1(13.52)Ch327.5(4.95)I	36.4	70.4	_	5.79
8IB	C210.8(8.83)S255.9(9.54)N324.6(4.50)I	44.5		69.7	6.32
8IC	C194.3(10.5)S250.2(6.91)N313.5(5.70)I	55.9		62.9	6.83
8ID	C171.4(6.75)S247.0(8.75)N304.8(6.91)I	75.6		57.8	7.34
8IIA	C227.4(5.45)Sc*273.8(12.7)Ch331.9(4.20)I	46.4	58.1		5.77
8IIB	C221.0(8.41)S270.7(6.60)N328.1(7.54)I	49.7		57.4	6.24
8IIC	C213.6(7.30)S267.8(5.41)N315.5(7.45)I	54.2		47.7	6.92
8IID	C187.7(6.50)S261.2(4.56)N307.3(6.84)I	73.5	_	46.1	7.30

Table 1 Phase transition temperatures, enthalpy changes, phase length of mesomorphic, and molecular length to diameter ratio (L/D) for the compounds 8 ^{*a*}

^a C: crystal; Sc^{*}: chiral smectic C; S: smectic; Ch: cholesteric; N: nemetic; I: isotropic.

morphic texture on the POM. The phase transition temperature and their enthalpy changes, phase length of liquid crystal phase and L/D of 8 are presented in Table 1. It can be observed that there are three endothermic peaks on the DSC curve of 8IA shown in Figure 1, in which the maximum of the first peak is 220.7 °C, the second is 257.1 °C and the third is 315.5 °C. For POM investigation it was found that the sample began melting near 215 °C in the POM experiment and showed typical lined texture of the chiral smectic phase after melting. The smectic phase transferred to cholesteric phase with the temperature increasing to 265 °C and looked as oily streak texture. Moreover, when the temperature was increased to 320 °C, birefraction disappeared and became isotropic. On the other hand, birefraction appeared again, the transition temperature of liquid crystalline phase and its corresponding texture could be observed during the slow process of decreasing temperature. The photographs are shown in Figure 2. In the case



Figure 1 The DSC cure of compounds 8 (the first heating rate:10 $^{\circ}C/min$).



Figure 2 Polarizing optical micro-graphs of **8IA**. (a) lined texture of chiral smetic C phase at 235 °C (\times 20); (b) oily streak texture of cholesteric phase at 271 °C (\times 20).

of **8IB**, focal-conics of smectic phase and Schlieren texture of nematic phase were observed from POM images. The POM pictures of **8IC** and **8ID** are similar to those of **8IB**.

All the liquid crystalline textures of **8IIA**, **8IIB**, **8IIC** and **8IID** obtained from POM are similar to those of **8IA**, **8IB**, **8IC** and **8ID**.

The relation-ship between the chemical structures and the liquid crystalline properties

The molecular length to diameter ratio (L/D) of the small molecular compound is important to the form of liquid crystal. Usually it is considered that the L/D ratio must be larger than 4 for the rigid rod molecules. According to Corey-Pauling-Koltun (CPK) molecular modeling, the L/D ratios of the compounds **8** in this work are in the range of 5.79—7.30.

From the results shown in Table 1, it is clear that the melting points and clearing points of **8IA** to **8ID**,

Schiff base

8IIA to **8IID** decreased gradually with the increasing of carbon number in the end alkoxyl group. However, the smectic phase length and smetic-nemetic phase transition temperature increased gradually, the nemectic phase length decreased. The melting point and clearing point of *trans*-conformation compounds **8II** are higher than those of *cis*-conformation compounds **8I** due to its higher symmetry.

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