

## Syntheses and Thermal Properties of New Liquid Crystals Bearing a Crown Ether Ring: Cation Binding in the Nematic Phase<sup>1</sup>

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A series of crown ether derivatives containing a biphenyl or cholesteryl moiety have been synthesized for the first time. The structural effects of these compounds on the formation of liquid-crystalline phases are discussed. We have found that benzo crown ether derivatives bearing a *p*-cyano- or *p*-(octyloxy)biphenyl moiety linked by an ester or ethyne group display a nematic liquid-crystalline phase, and 4'-((cholesteryloxy)carbonyl)benzo crown ethers exhibit a cholesteric phase; similar compounds with an oxymethyl-15-crown-5 or azacrown ether unit show no mesophases. For the biphenyl-type liquid crystals the effect of a 15-crown-5 ring on the thermal properties is similar to that seen with one lateral methoxy group, i.e., it decreases the thermal stability of the liquid-crystalline state, but the presence of an 18-crown-6 ring can exert a relatively large effect. These observations may be explained by the conformational rigidity of benzo crown rings, especially for benzo-15-crown-5, and their efficient participation in the entire conjugated system. Picrate doping experiments provided clear evidence for the selective binding of alkali-metal cations by the crown ethers in the nematic liquid-crystalline phase, although the complexation behavior of the crown ethers in this microenvironment is different from that seen in typical solvents. This is the first example of the formation of a liquid-crystalline phase in crown ether compounds and of host-guest-type behavior for such compounds in the liquid-crystalline state.

In addition to the traditional study of the binding abilities of crown ethers and their applications, many efforts have been directed toward the utilization of crown ethers as selective ionophoric units in other functionalized compounds. For example, Tundo et al.<sup>2</sup> showed that when complexed with silver(I), a surfactant analogue of azacrown ether aggregates spontaneously in aqueous solutions to form vesicles and that photoinduced electron transfer from sensitizers to the complex leads to the production of zerovalent silver which is stabilized by the microenvironment of the vesicles. Amphiphiles bearing a crown ether unit as a hydrophilic head group can form stable bilayer membranes that show a specific change in the aggregate state on the addition of metal cations in aqueous solutions,<sup>3</sup> a magnetically anisotropic cast film prepared from an aqueous solution containing single-chain amphiphiles with a Cu(II)-cyclam head group was described by Kunitake et al.<sup>4</sup> These studies suggest that a good combination of crown ether unit and amphiphile may provide a possibility for preparing new functionalized materials, while at the same time opening a new research field, i.e., the study of ion complexation in a special environment. The results that come out of this new field would be of importance for both biochemistry and materials science. On the other hand, there has been much interest in new liquid-crystalline materials because of their physicochemical properties as well as potential applications. Many metal complexes, e.g., bis( $\beta$ -diketonato)copper(II) complexes, have been known to show liquid-crystalline properties.<sup>5</sup> Substituted metallophthalocyanines display a discotic mesophase and may be candidates for liquid-crystalline one-dimensional conductors.<sup>6</sup> Lehn et al.<sup>7</sup> reported that the hexakis(*p*-(*n*-dodecyloxy)benzoyl) derivatives of the macrocyclic polyamines show a tubular mesophase. Thus, of particular interest is the possibility of combining the complexing properties of crown ethers with the supramolecular arrangements provided by the mesophases of liquid-crystalline compounds. In this study new liquid-crystalline compounds bearing a crown ether ring were synthesized, and their properties were studied from various

viewpoints. The following basic problems, which may be of concern to chemists studying crown ethers as well as to those interested in liquid-crystalline materials, were considered in the studies: (1) What is the effect of the introduction of a crown unit into liquid-crystalline compounds on their thermal properties? (2) What is the complexation behavior of the crown ether unit in the liquid-crystalline state?

Since the application of liquid crystals in numerical displays was found 20 years ago, numerous new liquid-crystalline compounds have been synthesized for this purpose. Schiff base liquid crystals, such as *p*-methoxybenzylidene-*p*'-butylaniline (MBBA), were the first examples of these compounds.<sup>8</sup> Since then, phenyl benzoate and cyanobiphenyl liquid crystals have been developed, which are more stable than MBBA. Among them *p*-*n*-alkyl-*p*'-cyanobiphenyl compounds are known to be excellent liquid crystals for display devices because of their suitable transition temperatures and low viscosity.<sup>9</sup> Aside from the nematic liquid crystals developed for display devices, cholesteric liquid crystals are also interesting compounds. Their particular supramolecular arrangements and other properties, especially the color changes that they can undergo, have been extensively studied and utilized in both chemistry and physics.<sup>10</sup> In the present

(1) Preliminary communication: He, G.-X.; Wada, F.; Kikukawa, K.; Matsuda, T. *J. Chem. Soc., Chem. Commun.* 1987, 1294-1296.

(2) Monserrat, K.; Grätzel, M.; Tundo, P. *J. Am. Chem. Soc.* 1980, 102, 5527-5529.

(3) (a) Shinkai, S.; Nakamura, S.; Manabe, O.; Yamada, T.; Nakashima, N.; Kunitake, T. *Chem. Lett.* 1986, 49-52. (b) Gu, X.-P.; Ikeda, I.; Okahara, M.; Kim, J. *Chem. Lett.* 1986, 1715-1718.

(4) Ishikawa, Y.; Tsukamoto, M.; Kunitake, T. *Chem. Lett.* 1986, 1181-1184.

(5) Ohta, K.; Ishii, A.; Yamamoto, I.; Matsuzaki, K. *J. Chem. Soc., Chem. Commun.* 1984, 1099-1101.

(6) Piechocki, C.; Simon, J.; Skoulios, A.; Guillon, D.; Weber, P. *J. Am. Chem. Soc.* 1982, 104, 5245-5247.

(7) Lehn, J.-M.; Malthete, J.; Levelut, A.-M. *J. Chem. Soc., Chem. Commun.* 1985, 1794-1796.

(8) Kelker, H.; Scheurle, B. *Angew. Chem.* 1969, 81, 903-904; *Angew. Chem., Int. Ed. Engl.* 1969, 8, 884-885.

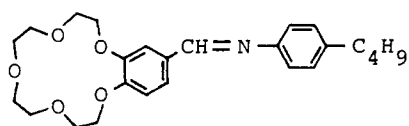
(9) Gray, G. W.; Harrison, K. J.; Nash, J. A. *Electron. Lett.* 1973, 9, 130-131.

(10) (a) Moseley, M. E.; Poupko, R.; Luz, Z. *Mol. Cryst. Liq. Cryst.* 1983, 95, 279-285. (b) Makow, D. *Mol. Cryst. Liq. Cryst.* 1983, 99, 117-122. (c) Tanaka, Y.; Chiyo, T.; Iijima, S.-I.; Shimizu, T.; Kusano, T. *Mol. Cryst. Liq. Cryst.* 1983, 99, 255-266.

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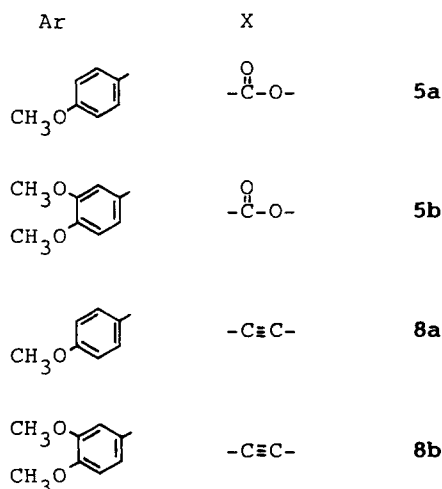
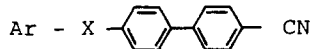
Chart I

A crown ether compound similar to MBBA:



1

Reference compounds:

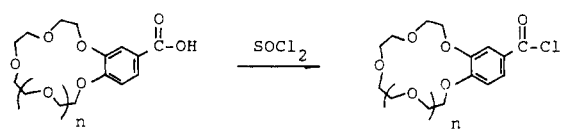


investigation a similarly structural approach was directed toward the synthesis of liquid-crystalline compounds containing a crown ether unit. Since compound 1 (Chart I) did not exhibit any mesophases, further investigations were focused on the preparation of compounds bearing *para*-substituted biphenyl groups. The ester and ethyne group were chosen as the linking group between the benzo crown unit and biphenyl moiety, except in the azacrown ether analogues, where a methylene group was used for synthetic reasons.

### Results and Discussion

**Synthesis.** *Para*-substituted phenyl benzoates bearing a crown ether ring were easily prepared by treating 4'-(chlorocarbonyl)benzo crown ethers with the corresponding *para*-substituted phenols (Scheme I). *p*-(*p*-(Octyloxy)phenyl)phenol (4f) was obtained from the reaction of 4,4'-dihydroxybiphenyl with 1 equiv of octyl bromide in the presence of KOH (34% yield). The synthesis of *p*-(*p*-heptylphenyl)phenol (4h) was carried out according to the following reaction sequences. *p*-Heptyl-*p*'-acetylbiphenyl was prepared from acetylation of *p*-heptylbiphenyl with acetic anhydride in nitrobenzene using AlCl<sub>3</sub> as catalyst (86%). Baeyer-Villiger oxidation of the ketone with peracetic acid (10% in acetic acid) at 60 °C for 10 h afforded *p*-heptyl-*p*'-acetoxybiphenyl (65%), which was then hydrolyzed to give 4h (90%).<sup>11</sup> 4i was prepared by Friedel-Crafts acylation of phenol with (*p*-hexylphenyl)-acetic acid chloride followed by reduction with triethylsilane in trifluoroacetic acid (in a 60% overall yield).<sup>12</sup>

Scheme I

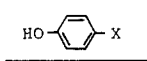


2a n = 1

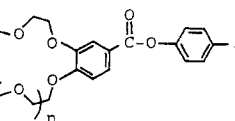
2b n = 2

3a n = 1

3b n = 2

4c X = *p*-C<sub>6</sub>H<sub>4</sub>-CN4d X = *p*-C<sub>6</sub>H<sub>4</sub>-CN

4e X = CN

4f X = *p*-C<sub>6</sub>H<sub>4</sub>-OC<sub>8</sub>H<sub>17</sub>4g X = C<sub>6</sub>H<sub>5</sub>4h X = *p*-C<sub>6</sub>H<sub>4</sub>-C<sub>7</sub>H<sub>15</sub>4i X = CH<sub>2</sub>CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>13</sub>

5c n = 1

5d n = 2

5e n = 1

5f n = 1

5g n = 1

5h n = 1

5i n = 1

The reaction described in Scheme II provides a convenient method for the preparation of tolan type compounds which are very attractive due to their potential application as new optical materials.<sup>13</sup> 4'-Ethynebenzo crown ethers were obtained by treating 4'-iodobenzo crown ethers with ethynyltrimethylsilane in the presence of Pd-(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> and CuI in diethylamine, followed by the hydrolysis with Na<sub>2</sub>CO<sub>3</sub> in methanol (in a 60% overall yield).<sup>14</sup> Alternatively, the ethynyl group can be introduced into the biphenyl part first, and coupling of the resulting *p*-ethynyl-*p*'-substituted-biphenyl with 4'-iodobenzo crown ethers under the same conditions then gives the products in similar yields.

The results of elemental analyses and IR spectra from several independent experiments showed that the solid samples of 19a (Scheme VI) contain 0.5 equiv of water, which could not be removed by drying under reduced pressure at room temperature. It seems that the water molecule is encapsulated by the crown ether moiety in 19a.

**Thermal Properties of the "Crowned" Liquid Crystals.** The thermodynamic stability of liquid-crystalline phases can be characterized in terms of a clearing point (*T*<sub>NI</sub>), i.e., the temperature at which the energy content of the anisotropic and isotropic liquids is equal. Comparison of the clearing points between compounds of analogous structure, differing only in one particular part of the molecule, permits assignment of the contribution of such structural features to the properties of the compounds as liquid crystals. The effect of the introduction of one crown ring into the liquid-crystalline molecules on their thermal properties are discussed in terms of a comparison to reference compounds (5a and 5b in Chart I), which contain one or two methoxy groups in the position corresponding to that occupied by the crown ether ring.

In Figure 1 it is seen that a substantial degree of supercooling was observed for the mesophase-to-solid transitions for both 5c and 14b. For compound 5c, the clearing point was found only during the cooling run of the DSC and the transition of K<sub>1</sub> to K<sub>2</sub>, as shown in Table I, was

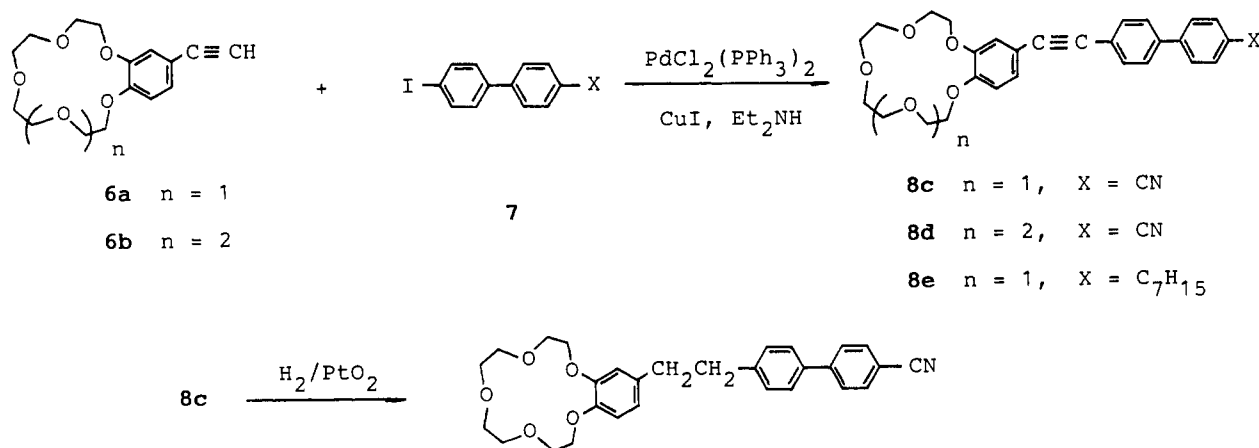
(11) Wada, F.; Arata, R.; Goto, T.; Kikukawa, K.; Matsuda, T. *Bull. Chem. Soc. Jpn.* 1980, 53, 2061-2063.

(12) West, C. T.; Donnelly, S. J.; Kooistra, D. A.; Doyle, M. P. *J. Org. Chem.* 1973, 38, 2675-2681.

(13) (a) Kurihara, T.; Tabei, H.; Kaino, T. *J. Chem. Soc., Chem. Commun.* 1987, 959-960. (b) Fouquey, C.; Lehn, J.-M.; Malthete, J. *J. Chem. Soc., Chem. Commun.* 1987, 1424-1426.

(14) Kikukawa, K.; He, G.-X.; Abe, A.; Goto, T.; Arata, R.; Ikeda, T.; Wada, F.; Matsuda, T. *J. Chem. Soc., Perkin Trans. 2* 1987, 135-141.

## Scheme II

Table I. Transition Temperatures of Phenyl Benzoate Liquid Crystals (5a-i)<sup>a</sup>

compd	trans temp, °C	compd	trans temp, °C
5a	K $\xrightarrow{148}$ N $\xrightarrow{320}$ I	5f	K $\xrightarrow{157}$ I
5b	K $\xrightarrow{191}$ N $\xrightarrow{198}$ I		K $\xrightarrow{122}$ N $\xrightarrow{148}$ I
5c	K1 $\xrightarrow{145}$ K2 $\xrightarrow{184}$ I	5g	mp 175–176 <sup>b</sup>
	K1 $\xrightarrow{130}$ N $\xrightarrow{186}$ I	5h	mp 158–160 <sup>b</sup>
5d	K1 $\xrightarrow{140}$ K2 $\xrightarrow{183}$ I	5i	mp 103–105 <sup>b</sup>
	K1 $\xrightarrow{120}$ N $\xrightarrow{154}$ I		
5e	mp 149–150 <sup>b</sup>		

<sup>a</sup>K, N, and I represent crystal, nematic, and isotropic phases, respectively. <sup>b</sup>5e,g-i do not show any mesophases.

not observed in the DSC chart, although the optical textures were different. Compound 14b shows a new exothermic peak in the cooling run of the DSC chart, which indicates the formation of a new mesophase, but the corresponding changes in optical texture were not found. The mesophases observed for compounds 5 and 8 were assigned tentatively to the nematic structure on the basis of "schlieren" or "marbled" textures observed upon placement of the mesophase between crossed polarizers. No smectic phase was observed for compounds 5 and 8 in their textures, which is consistent with the conclusion that the presence of a lateral group in the liquid-crystalline compounds eliminates the smectic phase.<sup>15</sup>

Gray et al. reported that the clearing point of 4-(methoxyphenyl)-4'-cyano-1,1'-biphenyl-4-carboxylate, a compound very similar to 5a, is 315 °C,<sup>16</sup> which is almost the same as that of 5a. Introduction of a methoxy group into the meta position of the benzoate ring not only decreases the clearing point ( $T_{NI}$ ) but also increases the melting point ( $T_{KN}$ ), rendering the nematic range of 5b much more narrow than that of 5a. This result is consistent with that reported previously and can be explained by the presence of the lateral methoxy group.<sup>15</sup> As shown in Table I, however, the clearing point ( $T_{NI}$ ) of 5c is similar to that of 5b, although the benzo-15-crown-5 unit is much larger than the dimethoxyphenyl unit. It is known that replacement of the alkoxy wing group in liquid crystals with

8f

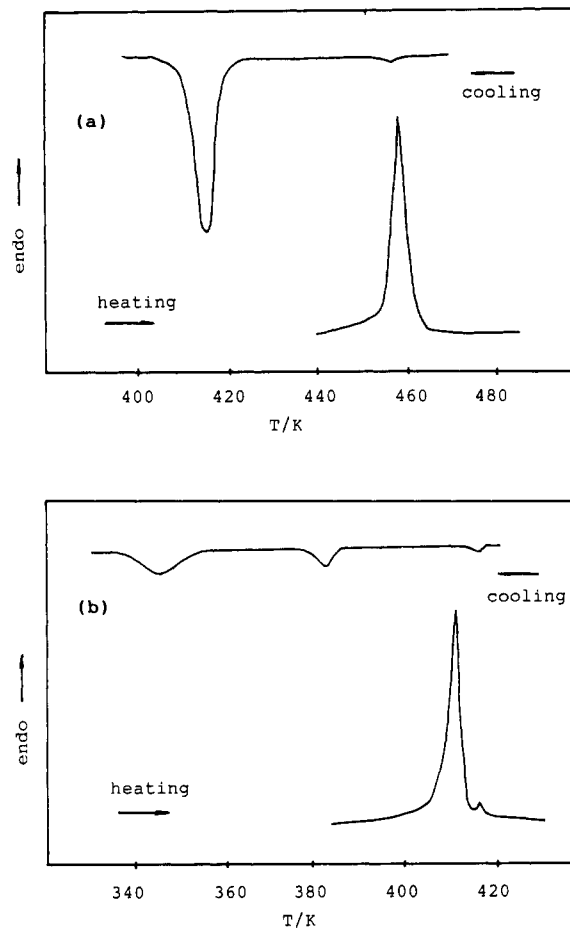


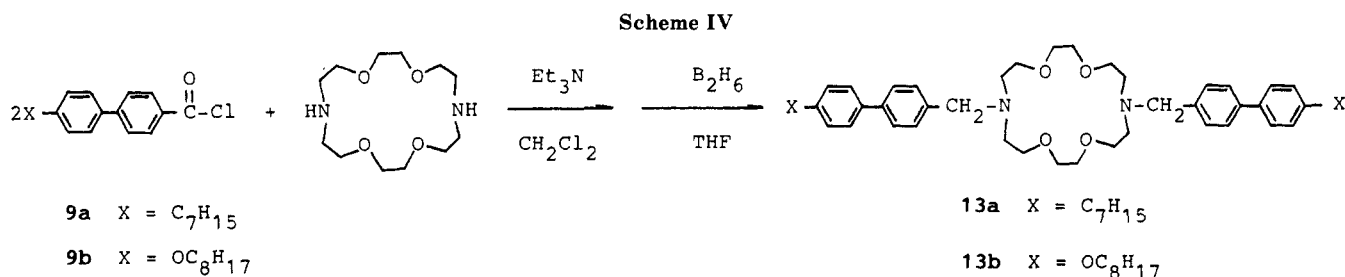
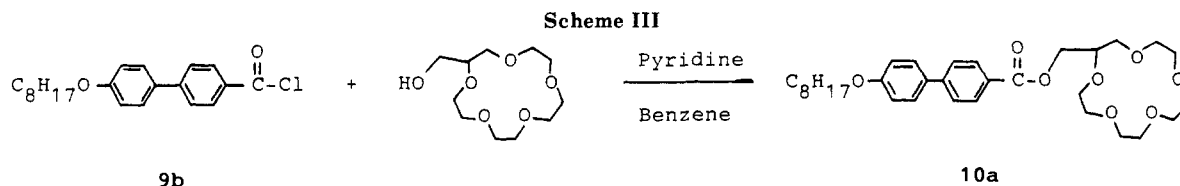
Figure 1. DSC thermogram of compounds 5c (a) and 14b (b).

an oxyethylene group decreases the thermodynamic stability of the liquid crystal and that the more oxygen atoms present in the wing group, the lower the clearing point of the liquid crystal.<sup>17</sup> In view of these results, it appears that the benzo-15-crown-5 unit is fairly rigid in its conformation and exerts an effect only on the thermal properties of the liquid crystals, similar to that seen with the smaller dimethoxyphenyl group. When the benzo-15-crown-5 unit is replaced by a benzo-18-crown-6 unit, the clearing point of 5d is indeed lower than that of 5c. Benzo-18-crown-6 is larger and is known to be more flexible

(15) (a) Subramanya Raj Urs, M.; Surendranath, V. *Mol. Cryst. Liq. Cryst.* 1983, 99, 279–284. (b) Gallardo, H.; Silva, F. C. *J. Chem. Soc., Perkin Trans. 2* 1987, 319–321.

(16) Coates, D.; Gray, G. W. *Mol. Cryst. Liq. Cryst.* 1975, 31, 275–283.

(17) Japanese Patents 57-46952, 57-99542, 57-108056.

**Table II. Transition Temperatures of Tolan Liquid Crystals (8a-e)<sup>a</sup>**

compd	trans temp, °C	compd	trans temp, °C
8a	K $\xrightleftharpoons{202}$ N $\xrightleftharpoons{284}$ I	8d	K $\xrightarrow{181}$ I
8b	K $\xrightleftharpoons{182}$ N $\xrightleftharpoons{202}$ I		K $\xrightleftharpoons{122}$ N $\xrightleftharpoons{162}$ I
8c	K $\xrightarrow{218}$ I	8e	mp 168-170 <sup>b</sup>
	K $\xrightarrow{165}$ N $\xrightleftharpoons{202}$ I	8f	mp 144-146 <sup>b</sup>

<sup>a</sup> K, N, and I represent crystal, nematic, and isotropic phases, respectively. <sup>b</sup> 8e,f do not show any mesophases.

than benzo-15-crown-5, although its cation-binding ability is much greater. The effect of wing groups can also be seen in Table I. The compound **5e**, with a *p*-cyanophenyl group, did not show any mesophase. The octyloxy wing group causes the compound **5f** to exhibit a monotropic nematic phase, but the *n*-heptyl group in **5h** results in the disappearance of the mesophase. Similar results are obtained for compound **5i**, although the molecule is longer.<sup>18</sup> It would be reasonable to assume that the presence of a benzo crown ether unit increases the width of the molecule and weakens the interaction between molecules. Consequently, a more polar wing group and a longer rigid core would probably be necessary in these compounds to obtain a mesophase.

Table II shows the structures and transition temperatures of the tolan type liquid crystals. The clearing points of the tolan derivatives presented here are higher than those of the phenyl benzoate derivatives in Table I. This result can be understood by reasoning that the ethyne central linkage favors conjugation over the whole rigid core and in addition renders the molecule more linear. The effects of the introduction of the crown unit and an alkyl wing group were also observed in this system, and the clearing point of **8c** is the same as that of **8b**. Replacement of the ethyne group with a dimethylene central linkage eliminates the mesophase as can be seen in **8f**.

From the results of the two systems with oxycarbonyl and ethynyl linkages it is clear that the thermodynamic stabilities of these liquid crystals are high, but the problem remains that the melting points of these compounds are also very high. Several structural modifications were introduced in efforts to lower the melting points of these compounds. One such attempt involved the introduction of a bent central group, such as a dimethylene linkage, into

**Table III. Transition Temperatures of *p*-(*p*-Substituted phenyl)benzoic Acid Derivatives 10a, 13a, and 13b**

compd	trans temp, °C
10a	mp 40-42 <sup>a</sup>
13a	mp 77-78 <sup>a</sup>
13b	mp 90-91 <sup>a</sup>

<sup>a</sup> 10a and 13a,b do not show any mesophases.

**Table IV. Transition Temperatures of Cholesterol Liquid Crystals 14a, 14b, and 19a<sup>a</sup>**

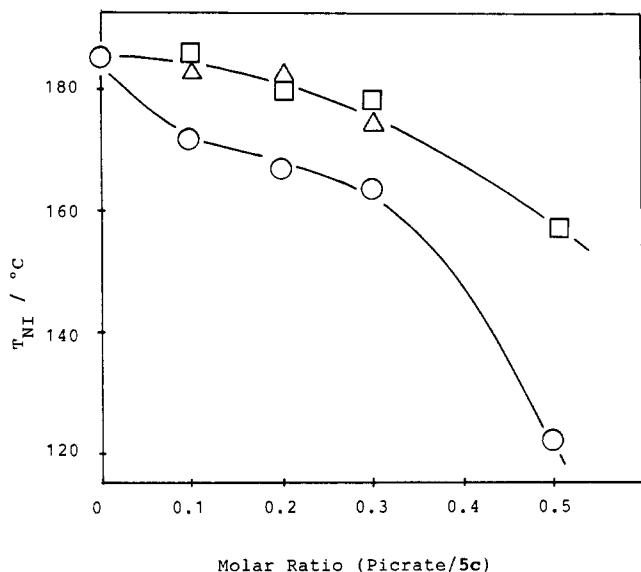
compd	trans temp, °C
14a	K $\xrightarrow{182}$ I
	K $\xrightleftharpoons{125}$ Ch $\xrightleftharpoons{165}$ I
14b	K $\xrightleftharpoons{133}$ Ch $\xrightleftharpoons{143}$ I
19a	mp 51-53 <sup>b</sup>

<sup>a</sup> K, Ch, and I represent crystal, cholesteric, and isotropic phases, respectively. <sup>b</sup> 19a does not show any mesophases.

the molecule, but this remedy failed, as described above. Another involved replacement of the benzo crown ether unit by a more flexible crown ether unit, e.g., 15-crown-5 or diaza-18-crown-6 (Schemes III and IV). As shown in Table III, however, the compounds **10a**, **13a**, and **13b** did not show any mesophases, although both **13a** and **13b** are very long molecules. As described earlier, Lehn et al. prepared the hexakis(*p*-(*n*-dodecyloxy)benzoyl) derivatives of the macrocyclic polyamines which show a tubular mesophase.<sup>7</sup> However, the macrorings in such compounds cannot act as cyclic ligands for cations because the nitrogen atoms are present as part of amide groups. In the synthesis of the compound **13**, which contains a diaza-18-crown-6 ring, we hoped that the loss of rigidity in **13** as compared to Lehn's compound could be compensated by using two long biphenyl moieties, but **13** still did not exhibit any liquid-crystalline phases. It seems that compounds containing a benzo crown ether unit form nematic liquid-crystalline phases not only due to the rigidity of the crown ring but also as a consequence of conjugation over the entire molecule, including the benzo crown ether unit.

The liquid-crystalline properties of cholesterol derivatives are shown in Table IV. Those containing a benzo crown ether unit (**14a** and **14b**) proved to exhibit a cholesteric phase, which was confirmed by DSC analysis and by comparison with the texture formed by cholesterol bromide. Replacement of the benzo-15-crown-5 unit by benzo-18-crown-6 decreases not only the clearing point but also the melting point. Interestingly, the compound **14b**

(18) Tinh, N. H.; Zann, A.; Dubois, J. C. *Mol. Cryst. Liq. Cryst.* **1979**, *53*, 29-41, 43-54.



**Figure 2.** Effect of picrate doping on the nematic-isotropic transition temperature ( $T_{NI}$ ) of **5c**:  $\circ$ , sodium picrate;  $\square$ , potassium picrate;  $\Delta$ , tetramethylammonium picrate.

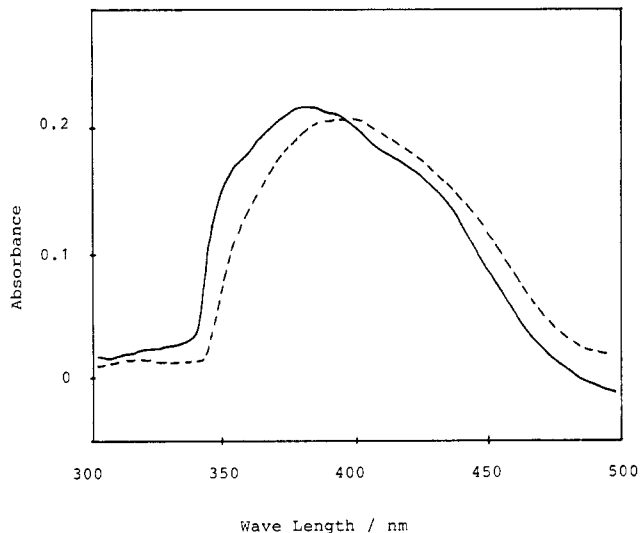
**Table V. Absorption Maxima in UV Spectra of Picrate-Doped **5c** or **5d**<sup>a</sup>**

compd	$\lambda_{max}$ of picrates in isotropic phase (in nematic phase), nm		
	NaPi	KPi	$(CH_3)_4NPi$
<b>5c</b>	380 (390)	385 (385)	385 (385)
<b>5d</b>	385 (385)	385 (410)	385 (385)

<sup>a</sup> UV spectra were measured by a multichannel spectrophotometer (Otsuka Electronics, MCPD-100) equipped with a hot plate; thickness of samples 50–80 nm.

with a benzo-18-crown-6 unit shows an enantiotropic cholesteric phase. However, the analogue containing a monoaza-15-crown-5 (**19a**) did not exhibit a mesophase. Gokel et al.<sup>19</sup> synthesized *N*-((cholesteryloxy)carbonyl)-aza-15-crown-5, a compound closely related to **19a**, and a series of compounds with similar structures, but formation of a mesophase was not reported for these compounds although it is known that such steroidal lariat ethers can aggregate in water to form nonionic liposomes.<sup>20</sup>

**Picrate-Doping Study.** When the liquid crystals **5c** and **5d** are doped with picrates, their nematic melts tend to supercool for a long time even at room temperature, although the viscosity is very high. The melt (pseudoisotropic liquid) appears yellow due to the picrate with which the compound was doped. Depression of the clearing point ( $T_{NI}$ ) for **5c** with increasing concentration of picrate is shown in Figure 2. Since tetramethylammonium ion cannot be complexed by the benzo-15-crown-5 unit, the depression of  $T_{NI}$  by doping with potassium and tetramethylammonium picrates should be considered as arising simply from the addition of an impurity to the liquid crystals. On the other hand,  $T_{NI}$  was decreased markedly on doping with sodium picrate, probably due to the selective complexation of the crown ether unit with sodium cation. Binding a cation to the crown unit will decrease the anisotropy of polarizability of the molecule and produce a steric effect that hinders



**Figure 3.** UV spectra of sodium picrate doped **5c** in the nematic liquid-crystalline phase (---) and in the isotropic liquid phase (—); molar ratio of sodium picrate/**5c** = 5/1000.

molecular packing. Both factors could lower the thermodynamic stability of the liquid crystals, along with the impurity effect caused by the picrates present as an impurity.

Selective binding in the liquid-crystalline phase can also be observed by UV measurement (Figure 3 and Table V). Doping of **5c**, which contains a benzo-15-crown-5 unit, with sodium picrate led to a red shift ( $\lambda_{max}$  from 380 to 390 nm) when **5c** changed from an isotropic liquid phase to a nematic liquid-crystalline phase, but potassium and tetramethylammonium picrates did not cause such a shift. A similar shift was found when **5d** was doped with potassium picrate, but not with sodium and tetramethylammonium picrates. A red shift in the absorption of picrates in solution is commonly associated with the formation of separated ion pairs in complexation with crown ethers.<sup>21</sup> Thus, the red shift observed in the nematic phase can reasonably be explained by the formation of a similarly separated ion pair between the complexed cation and picrate anion, restricted by the liquid-crystalline molecules in the nematic phase.

It is well-known that the preferential complexation of  $K^+$  by the 18-crown-6 ring is a good example of the hole size-ionic diameter relationship, but the complexation of  $Na^+$  by 15-crown-5 is not as strong, in spite of the fact that the size of  $Na^+$  is close to the hole size of the 15-crown-5 ring.<sup>14,22</sup> This dichotomy has been discussed in terms of the high hydration energy of  $Na^+$  cation as well as other reasons.<sup>23</sup> On the other hand, the 15-crown-5 ring can form an intermolecular sandwich complex with  $K^+$  cation in both two-phase and homogenous systems.<sup>14</sup> In the present case, however, the cation-binding behavior seems to follow the hole size-ionic diameter relationship, i.e., benzo-18-crown-6 gives the best binding to  $K^+$  and benzo-15-crown-5 with  $Na^+$ . This result can be understood in terms of the different solvation environments for the cations in this case and in common solvents. In common

(19) Gokel, G. W.; Hernandez, J. C.; Viscariello, A. M.; Arnold, K. A.; Campana, C. F.; Echegoyen, L.; Fronczek, F. R.; Gandour, R. D.; Morgan, C. R.; Trafton, J. E.; Miller, S. R.; Minganti, C.; Eiband, D.; Schultz, R. A.; Tamminen, M. *J. Org. Chem.* **1987**, *52*, 2963–2968.

(20) Echegoyen, L. E.; Hernandez, J. C.; Kaifer, A. E.; Gokel, G. W.; Echegoyen, L. *J. Chem. Soc., Chem. Commun.* **1988**, 836–837.

(21) (a) Wong, K. H.; Yagi, K.; Smid, J. *J. Membr. Biol.* **1974**, *18*, 379–397. (b) Wada, F.; Wada, Y.; Goto, T.; Kikukawa, K.; Matsuda, T. *Chem. Lett.* **1980**, 1189–1192. (c) Inoue, Y.; Fujiwara, C.; Wada, K.; Tai, A.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1987**, 393–394.

(22) Gokel, G. W.; Goli, D. M.; Minganti, C.; Echegoyen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786–6788.

(23) (a) Izatt, R. M.; Christensen, J. J. *Synthetic Multidentate Macrocyclic Compounds*; Academic Press: New York, 1987. (b) Vögtle, F. *Host Guest Complex Chemistry I*; Springer-Verlag: Berlin, 1981.

solvents complexation is always competitive with solvation, but in this case complexation occurs under neat conditions, and a "neat" effect between the crown ethers and cations may be observed. At present, no evidence could be found for the formation of such a sandwich complex in the liquid-crystalline phase, since formation of the sandwich complex would make benzo-15-crown-5 show  $K^+$  selectivity, and a large red shift in the UV spectra of the picrate would be observed.<sup>14,21</sup>

### Conclusion

The present study demonstrates that benzo crown ether derivatives bearing a para-substituted biphenyl group display a nematic liquid-crystalline phase, and 4'-(cholesteryloxy)carbonylbenzo crown ethers give a cholesteric liquid-crystalline phase, while similar compounds with a 15-crown-5 or azacrown ether unit show no mesophases. The result may be explained by the conformational rigidity of benzo crown rings and their effective participation in the entire conjugated system. For the biphenyl type liquid crystals the effect of 15-crown-5 ring on the thermal properties was comparable with that of one lateral methoxy group, while 18-crown-6 ring gives a relatively large effect. The results obtained suggest that relatively long rigid conjugation cores and polar wing groups are both necessary for these compounds to exhibit liquid-crystalline phases. Picrate-doping experiments showed that selective binding of the crown ethers with alkali-metal cations also occurs in the nematic liquid-crystalline phase. However, the complexation behavior of crown ethers in such a micro-environment is different with that in usual solvents as reported previously. For example, benzo-15-crown-5 exhibits  $Na^+$  selectivity and no 2:1 crown unit:cation complex forms under such conditions.

### Experimental Section

**General Procedures.** All solvents and reagents were of reagent grade quality, were commercially available, and were used without further purification, except when noted. Pyridine, triethylamine, and diethylamine were dried over KOH, distilled, and stored over 4A molecular sieves. Ethanol was dehydrated over Mg and distilled before use. Diethyl ether, tetrahydrofuran (THF), and benzene were refluxed over Na, distilled, and stored under nitrogen atmosphere. Silica gel for column chromatography was microbead silica gel (grade 4B, 100–200 mesh, neutral, Kishida Chemical Ltd.). Alumina for column chromatography was Kishida activated alumina (300 mesh, pH = 10).

<sup>1</sup>H NMR spectra were recorded on a Hitachi R-24B (60 MHz) NMR spectrometer, and chemical shifts are expressed in ppm ( $\delta$  scale) downfield from internal tetramethylsilane (TMS). Mass spectra were measured on a JEOL JMS-QH100 mass spectrometer. IR spectra were recorded on a JASCO A-100 infrared spectrophotometer and were calibrated against the 1601-cm<sup>-1</sup> band of polystyrene. Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. All elemental analyses were performed at the Microanalytical Laboratory of the Faculty of Science, Kyushu University.

**Substituted Phenyl Benzoates Bearing a Crown Ether Ring. General Procedure.** The reactions and compounds concerned are summarized in Scheme I. 4'-(Hydroxycarbonyl)benzo crown ethers **2a** and **2b** were converted into the corresponding 4'-(chlorocarbonyl)benzo crown ethers **3a** and **3b** by heating with thionyl chloride under reflux. The products were identified by IR ( $\nu_{C=O}$  = 1750 cm<sup>-1</sup>) and used in the following reaction without purification.<sup>24</sup> The para-substituted phenols **4** were heated under reflux in dry benzene for 5 h with 4'-(chlorocarbonyl)benzo crown ethers in the presence of pyridine (2 equiv). After cooling, the resulting solution was washed with dilute

HCl, saturated aqueous Na<sub>2</sub>CO<sub>3</sub> and NaCl, successively, and dried over MgSO<sub>4</sub>. The solvent was evaporated to give the ester as a solid which was purified by recrystallization from acetone or benzene. The purity and structures were confirmed by IR, NMR, and elemental analysis. The reference compounds (**5a** and **5b** in Chart I) were synthesized by the same methods.

**5a:** white solid, yield 97%; mp 148–150 °C; IR (Nujol) 2220, 1725, 1260, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.9 (s, 3 H), 6.9–8.3 (m, 12 H). Anal. Calcd for C<sub>21</sub>H<sub>15</sub>O<sub>3</sub>N: C, 76.58; H, 4.59; N, 4.25. Found: C, 76.54; H, 4.60; N, 4.17.

**5b:** white solid, yield 67%; mp 190–191 °C; IR (Nujol) 2220, 1725, 1260, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.9 (s, 6 H), 6.8–7.9 (m, 11 H). Anal. Calcd for C<sub>22</sub>H<sub>17</sub>O<sub>4</sub>N: C, 73.53; H, 4.77; N, 3.90. Found: C, 73.59; H, 4.76; N, 3.81.

**5c:** white solid, yield 70%; mp 184–186 °C; IR (Nujol) 2200, 1720, 1200, 1130 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.5–4.5 (m, 16 H), 6.8–8.0 (m, 11 H). Anal. Calcd for C<sub>28</sub>H<sub>27</sub>O<sub>7</sub>N: C, 68.70; H, 5.56; N, 2.86. Found: C, 68.73; H, 5.57; N, 2.84.

**5d:** white solid, yield 40%; mp 185–187 °C; IR (Nujol) 2200, 1720, 1100 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.3–4.4 (m, 20 H), 6.8–7.9 (m, 11 H). Anal. Calcd for C<sub>30</sub>H<sub>31</sub>O<sub>8</sub>N: C, 67.53; H, 5.86; N, 2.63. Found: C, 67.19; H, 5.90; N, 2.58.

**5e:** white solid, yield 60%; mp 149–150 °C; IR (Nujol) 2200, 1720, 1120 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.5–4.5 (m, 16 H), 6.8–7.9 (m, 7 H). Anal. Calcd for C<sub>22</sub>H<sub>23</sub>O<sub>7</sub>N: C, 63.92; H, 5.61; N, 3.39. Found: C, 63.89; H, 5.53; N, 3.38.

**5f:** white solid, yield 63%; mp 156–158 °C; IR (Nujol) 1720, 1600, 1240, 1140 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.7–1.8 (m, 15 H), 3.6–4.4 (m, 18 H), 6.7–7.9 (m, 11 H). Anal. Calcd for C<sub>35</sub>H<sub>44</sub>O<sub>8</sub>: C, 70.92; H, 7.48. Found: C, 70.94; H, 7.51.

**5g:** white solid, yield 94%; mp 174–176 °C; IR (Nujol) 1720, 1200 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.4–4.4 (m, 16 H), 6.8–7.9 (m, 12 H). Anal. Calcd for C<sub>27</sub>H<sub>28</sub>O<sub>7</sub>: C, 69.81; H, 6.08. Found: C, 70.07; H, 6.13.

**5h:** white solid, yield 66%; mp 158–160 °C; IR (Nujol) 1720, 1210, 1140 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.9–1.8 (m, 13 H), 2.5–2.8 (t, 2 H), 3.5–4.3 (m, 16 H), 6.8–8.0 (m, 11 H). Anal. Calcd for C<sub>34</sub>H<sub>42</sub>O<sub>7</sub>: C, 72.52; H, 7.52. Found: C, 72.19; H, 7.44.

**5i:** white solid, yield 85%; mp 103–105 °C; IR (Nujol) 1720, 1200, 1140 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.7–2.0 (m, 11 H), 2.4–2.8 (t, 2 H), 2.9 (s, 4 H), 3.6–4.3 (m, 16 H), 6.7–7.9 (m, 11 H). Anal. Calcd for C<sub>35</sub>H<sub>44</sub>O<sub>7</sub>: C, 72.89; H, 7.69. Found: C, 72.38; H, 7.60.

### Biphenylethyne Derivatives Bearing a Crown Ether Ring.

**General Procedure.** The reactions and compounds concerned are shown in Scheme II. A solution of 4'-ethynylbenzo crown ethers **6a** and **6b**,<sup>14</sup> *p*-iodobiphenyl derivatives **7**,<sup>25</sup> 0.1 equiv of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, and CuI in diethylamine was refluxed for 24 h under nitrogen. After removal of the solvent, the residue was purified by passing through a short alumina column with chloroform as eluent, and recrystallization from acetone gave the product as a white solid. The reference compounds **8a** and **8b** (Chart I) were synthesized by the same methods. **8f** was obtained by hydrogenation of **8c** under atmospheric hydrogen in the presence of PtO<sub>2</sub> as catalyst at room temperature.<sup>26</sup> The purity and structures were confirmed by IR, NMR, and elemental analysis.

**8a:** white solid, yield 65%; mp 200–202 °C; IR (Nujol) 2210, 2190, 1600, 1240, 820 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.8 (s, 3 H), 6.7–7.7 (m, 12 H). Anal. Calcd for C<sub>22</sub>H<sub>15</sub>ON: C, 85.41; H, 4.89; N, 4.53. Found: C, 84.97; H, 4.94; N, 4.43.

**8b:** white solid, yield 79%; mp 180–182 °C; IR (Nujol) 2210, 2190, 1600, 1590, 820 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.9 (s, 6 H), 6.7–7.8 (m, 11 H). Anal. Calcd for C<sub>23</sub>H<sub>17</sub>O<sub>2</sub>N: C, 81.40; H, 5.05; N, 4.13. Found: C, 81.18; H, 5.03; N, 3.98.

**8c:** white solid, yield 80%; mp 218–220 °C; IR (Nujol) 2200, 1580, 1240, 1100 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.4–4.2 (m, 16 H), 6.6–7.9 (m, 11 H). Anal. Calcd for C<sub>29</sub>H<sub>27</sub>O<sub>5</sub>N: C, 74.18; H, 5.80; N, 2.98. Found: C, 74.11; H, 5.82; N, 3.02.

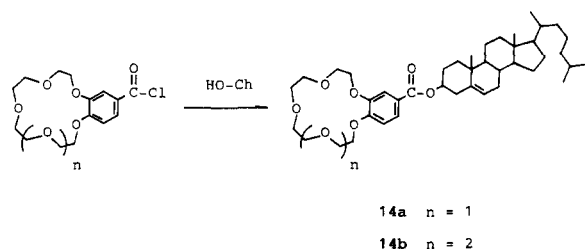
**8d:** white solid, yield 65%; mp 181–182 °C; IR (Nujol) 2220, 2200, 1250, 1120 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.5–4.3 (m, 20 H), 6.6–7.7 (m, 11 H). Anal. Calcd for C<sub>31</sub>H<sub>31</sub>O<sub>5</sub>N: C, 72.50; H, 6.08; N, 2.73. Found: C, 72.33; H, 6.07; N, 2.65.

(25) Wirth, H. O.; Königstein, O.; Kern, W. *Liebigs Ann. Chem.* **1960**, *634*, 84–104.

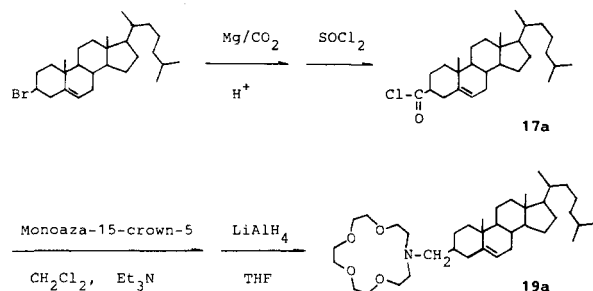
(26) Kikukawa, K.; Abe, A.; Wada, F.; Matsuda, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 961–962.

(24) Haines, A. H.; Hodgkinson, I.; Smith, C. *J. Chem. Soc., Perkin Trans. 1* **1983**, 311–318.

Scheme V



Scheme VI



**8e:** white solid, yield 79%; mp 168–170 °C; IR (Nujol) 2200, 1260, 1120  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.8–1.9 (m, 13 H), 2.4–2.8 (t, 2 H), 3.6–4.3 (m, 16 H), 6.6–7.7 (m, 11 H). Anal. Calcd for  $\text{C}_{35}\text{H}_{42}\text{O}_5$ : C, 77.46; H, 7.80. Found: C, 77.41; H, 7.77.

**8f:** white solid, yield 50%; mp 144–146 °C; IR (Nujol) 2200, 1240  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.9 (s, 4 H), 3.5–4.2 (m, 16 H), 6.6–7.8 (m, 11 H).

***p*-Substituted-phenyl Benzoates Carrying a Crown Ether Ring.** The reactions and compounds concerned are shown in Scheme III and IV.

**10a:** The procedure is similar to that described in the preparation of **5c**, and the product was purified by chromatography (silica gel/chloroform) and recrystallization from hexane.

**12a,b:** A solution of **9a** and **9b**, prepared from *p*-(*p*-substituted-phenyl)benzoic acid<sup>27</sup> and thionyl chloride [IR (neat)  $\nu_{\text{C=O}}$  = 1770, 1740  $\text{cm}^{-1}$ , two bands for both compounds], diaza-18-crown-6,<sup>28</sup> and triethylamine (5 equiv) in  $\text{CH}_2\text{Cl}_2$  was refluxed for 5 h. After cooling, the solution was washed with dilute HCl and saturated aqueous  $\text{Na}_2\text{CO}_3$  and NaCl, successively, and dried over  $\text{MgSO}_4$ . The solvent was removed by evaporation, and residue was recrystallized from heptane to give a white solid.

**13a,b:** **12a** and **12b** were reduced with  $\text{BH}_3$  according to the published method.<sup>29</sup> The products (**13a** and **13b**) were purified by recrystallization from ethanol.

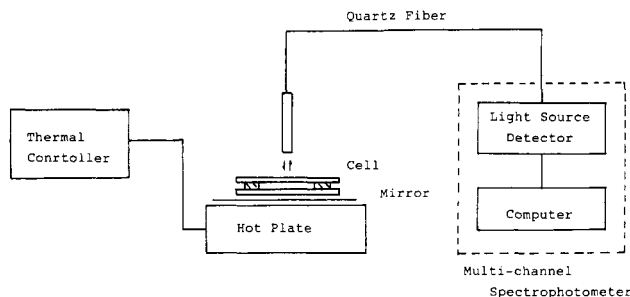
**10a:** white solid, yield 30%; mp 40–42 °C; IR (Nujol) 1760, 1640, 1300, 1140, 840  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.7–2.0 (m, 15 H), 3.1–4.5 (m, 23 H), 6.8–8.2 (m, 8 H); MS,  $m/e$  558 ( $\text{M}^+$ ).

**12a:** white solid, yield 76%; mp 127–128 °C; IR (Nujol) 1620, 1130, 1090, 810  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.8–2.0 (m, 26 H), 2.4–2.7 (t, 4 H), 3.3–3.9 (m, 24 H), 7.1–7.7 (m, 16 H).

**12b:** white solid, yield 65%; mp 142–144 °C; IR (Nujol) 1620, 1600, 1120, 1080, 830  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.6–2.0 (m, 30 H), 3.4–4.2 (m, 28 H), 6.7–7.9 (m, 16 H).

**13a:** white solid, yield 70%; mp 77–78 °C; IR (Nujol) 1500, 1120  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.7–2.0 (m, 26 H), 2.3–3.0 (tt, 16 H), 3.4–3.8 (t, 16 H), 7.0–7.6 (m, 16 H). Anal. Calcd for  $\text{C}_{52}\text{H}_{74}\text{O}_4\text{N}_2$ : C, 78.94; H, 9.43; N, 3.54. Found: C, 78.82; H, 9.49; N, 3.56.

**13b:** white solid, yield 69%; mp 90–91 °C; IR (Nujol) 1605, 1250, 1120, 1050, 830  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.7–2.0 (m, 30 H), 2.7–3.2 (t, 8 H), 3.5–4.2 (m, 24 H), 6.8–7.7 (m, 16 H). Anal. Calcd



**Figure 4.** Apparatus used in determining the UV spectra at high temperature.

for  $\text{C}_{64}\text{H}_{78}\text{O}_6\text{N}_2$ : C, 76.20; H, 9.24; N, 3.29. Found: C, 76.01; H, 9.04; N, 3.27.

**Cholesterol Derivatives Bearing a Crown Ether Ring.** The reactions and compounds concerned are shown in Schemes V and VI.

**14a** and **14b** were synthesized by the method used in preparing **5c**, and the products were purified by recrystallization from a mixed solvent (heptane:benzene 8:2).

**15a** (cholest-5-ene-3 $\beta$ -carboxylic acid) was prepared in 30% yield, mp 220–222 °C, by a modification of Roberts's method.<sup>30</sup> Cholesteryl bromide (6.7 mmol) was added to a solution of methylmagnesium iodide, prepared from methyl iodide (20 mmol) and magnesium (45 mmol) in dry ether (50 mL), and the mixture was refluxed for 20 h under nitrogen. After cooling, dry carbon dioxide gas was bubbled into the solution for 1 h, and the resulting solution was acidified by dilute HCl and treated in the usual way. The product was recrystallized from benzene to give a white solid.

**17a** (cholest-5-ene-3 $\beta$ -carboxylic acid chloride, 1.2 mmol), prepared from the reaction with thionyl chloride in benzene,<sup>31</sup> was refluxed with monoaza-15-crown-5 (1.2 mmol) and triethylamine (0.7 mL) in 10 mL of  $\text{CH}_2\text{Cl}_2$  for 10 h. The solution was cooled to room temperature, washed with dilute HCl, aqueous  $\text{Na}_2\text{CO}_3$ , and aqueous NaCl, successively, and dried over  $\text{MgSO}_4$ . Concentration of the solution gave the crude amide which was chromatographed on a column of silica gel/chloroform to give **18a** as a pale yellow solid. **19a** was obtained by reduction of the amide (**18a**) with  $\text{LiAlH}_4$  in dry THF (reflux for 10 h) and purified by chromatography (silica gel/chloroform-methanol).

**14a:** white solid, yield 86%; mp 178–180 °C; IR (Nujol) 1700, 1220, 1140  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{42}\text{H}_{64}\text{O}_7$ : C, 74.01; H, 9.47. Found: C, 73.81; H, 9.39.

**14b:** white solid, yield 66%; mp 124–125 °C; IR (Nujol) 1700, 1270, 1120  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{44}\text{H}_{68}\text{O}_8$ : C, 72.89; H, 9.45. Found: C, 72.75; H, 9.43.

**18a:** pale yellow solid, yield 90%; mp 66–70 °C; IR (neat) 2920, 2850, 1630, 1460, 1120  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.5–2.0 (m, 43 H), 2.5 (br s, 1 H), 3.4–3.9 (7, 20 H), 5.3 (br s, 1 H).

**19a:** pale yellow solid, yield 83%; mp 51–53 °C; IR (neat) 2920, 2850, 1460, 1130  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.7–2.0 (m, 44 H), 2.6–2.9 (t, 6 H), 3.5–3.8 (m, 16 H), 5.3 (br s, 1 H). Anal. Calcd for  $\text{C}_{38}\text{H}_{69}\text{O}_{4.5}\text{N}$  (**19a**·0.5 $\text{H}_2\text{O}$ ): C, 74.70; H, 11.22; N, 2.29. Found: C, 74.80; H, 11.05; N, 2.26.

**Measurements for Thermal and Optical Properties.** The thermal and optical properties were studied by using a differential scanning calorimeter (Rigaku-Denki, Model DSC8230B-TAS100) and a micromelting point apparatus equipped with a polarizer (Yanagimoto Ltd.). The transition temperatures are given in Tables I–IV. Figure 1, parts a and b, show the DSC chart of **5c** and **14b**, respectively, measured at the rate of 5 °C/min for both heating and cooling.

**Picrate-Doping Experiments.** Sodium, potassium, and tetramethylammonium picrates were used as doping agents. The picrate-doped sample was prepared by dissolving the picrate in dichloromethane solution of the crown ether compounds. After removal of the solvent under reduced pressure at room temperature, the resulting pale yellow solid was melted completely once before the subsequent measurements.

(27) Gray, G. W.; Hartley, J. B.; Jones, B. *J. Chem. Soc.* **1955**, 1412–1420.

(28) Gatto, V. J.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 8240–8244.

(29) Brown, H. C.; Heim, P.; Yoon, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 1637–1646.

(30) Roberts, G.; Shoppee, C. W.; Stephenson, R. J. *J. Chem. Soc.* **1954**, 2705–2715.

(31) Baker, R. H.; Squire, E. N. *J. Am. Chem. Soc.* **1948**, 1487–1492.



The thermal and optical properties of the liquid crystals doped by the picrates were examined by use of the micromelting point apparatus equipped with a polarizer. Figure 2 gives the effect of picrate doping on the clearing points ( $T_{NI}$ ) of 5c.

UV spectra of the picrate-doped liquid crystals containing a crown ether unit were measured by a multichannel spectrophotometer (Otsuka Electronics, MCPD-100) using a heated sample holder as shown in Figure 4. The sample cell is composed of two quartz plates and aluminum foil spacers (thickness 30–40 nm). The sample in the cell was heated to an isotropic state once before the measurement. The thickness of the sample was determined by a light interference method commonly used for thin film or thin IR cells with the same instrument in the melt state. The

sample thickness thus obtained is in the range 50–80 nm. Figure 3 shows examples of the UV spectra, and Table V gives a list of  $\lambda_{max}$  values for the UV spectra in the liquid-crystalline state or in the isotropic state.

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## Fluorescence and Absorption Studies of the Cation-Binding Behavior of "Crowned" Liquid Crystals in Solution and in the Nematic Phase

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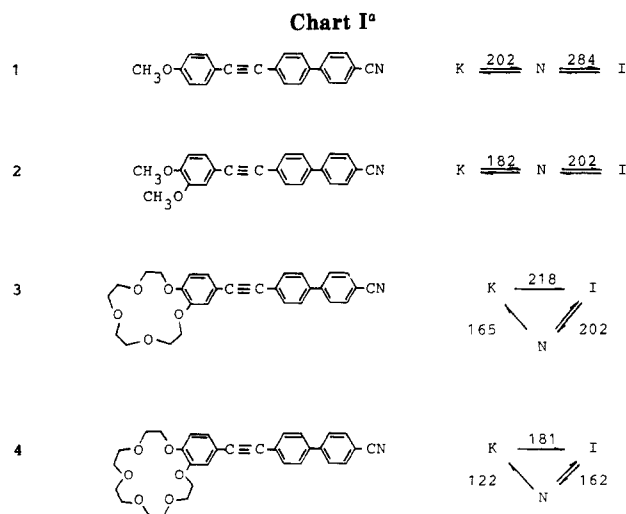
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4'-((p'-Cyanobiphenyl)ethynyl)benzo crown ethers (3 and 4) not only display a nematic liquid-crystal phase but also show very strong fluorescence, both in solution and in the liquid-crystalline state. The "crowned" liquid crystal compound 4 exhibited a bathochromic shift in fluorescence and a hypsochromic shift in absorption with increasing solvent polarity. The addition of alkali-metal cations produced hypsochromic changes in both the fluorescence and absorption of 4. The cation-induced effects (fluorescence, absorption, and fluorescence quenching with thiocyanate salts) have been used as aids in determining the cation-binding ability of 4 in polar solvents, producing results similar to those obtained from conventional methods. On the basis of solution studies, the binding abilities of 3 and 4 in a eutectic nematic liquid crystal (ZLI-2806) were determined. The results revealed that 3 and 4 also complex alkali-metal cations selectively in the nematic phase, and the cation-binding ability is comparable with that found in methanol solution, but no evidence for 2:1 crown unit:cation complexation of 3 with KSCN was obtained under the present conditions. On the other hand, an energy-transfer quenching study with sodium 3-perylenecarboxylate under the same conditions did not show any specific cation-crown ether interaction.

The absorption and fluorescence properties of crown ether compounds have been studied extensively, and many compounds referred to as "chromoionophores" or "fluoroionophores" have been synthesized.<sup>1</sup> Because of their high sensitivity and selectivity, fluoroionophores are often considered to be exceptionally convenient for the study of ion-binding behavior. For example, the phenolic fluoroionophores with umbelliferone units<sup>2</sup> and benzothiazolyphenols bearing a crown ether unit<sup>3</sup> are used in fluorometric determination of alkali- and alkaline-earth-metal cations in solutions. The anthracenoyl crown ethers have been used as fluorescent probes for the solid-phase transition of phosphatidylcholine,<sup>4</sup> and the diastereomeric complexation behavior of the chiral coronands was studied by means of their quenching phenomena.<sup>5</sup>

In previous papers we reported the syntheses and thermal properties of new liquid-crystalline compounds bearing a crown ether ring and demonstrated that the selective cation binding of crown ethers could also be observed in the liquid-crystalline state by a picrate doping experiment.<sup>6</sup> We also found that 4'-((p'-cyanobiphenyl)ethynyl)benzo crown ethers (3 and 4 in Chart I) not only display a nematic liquid crystal phase but also show a very strong fluorescence both in solutions and in the liquid-crystalline state.

The complexation behavior of various crown ethers has been observed primarily in solution; there are also many



<sup>a</sup> Transition temperature in °C. K, N, and I represent crystal, nematic, and isotropic phase, respectively.

studies on the solid-state structure of crown ether complexes. Recently the binding behavior of crown ethers in

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(1) (a) Lohr, H.-G.; Vögtle, F. *Acc. Chem. Res.* **1985**, *18*, 65–72. (b) Takagi, M.; Nakamura, H. *J. Coord. Chem.* **1986**, *15*, 53–82.  
 (2) Nishida, H.; Katayama, Y.; Katsuki, H.; Nakamura, H.; Takagi, M.; Ueno, K. *Chem. Lett.* **1982**, 1853–1854.  
 (3) Nakashima, K.; Nagaoka, Y.; Nakatsuji, S.; Kaneda, T.; Tanigawa, I.; Hirose, K.; Misumi, S.; Akiyama, S. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3219–3223.