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Chirality Recognition by a Color Change in Crowned Cholesteric Liquid Crystals

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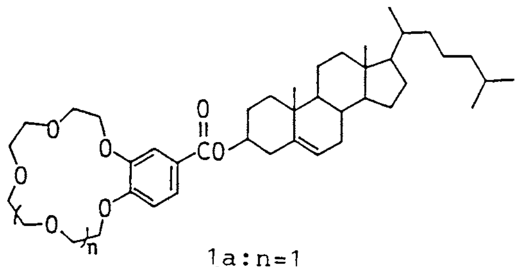
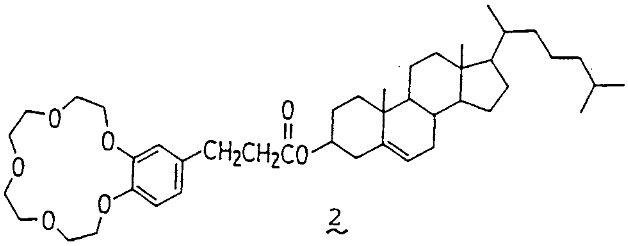
Alkali (R)- and (S)-mandelates can change the helical pitch of cholesteric liquid crystals containing steroidal crown ethers in an enantioselective manner. In certain cases the pitch difference between (R)- and (S)-mandelates can be detected visually as a color change in the liquid crystals.

Liquid crystals have been used as novel media for stereoselective reactions,1,2) investigations of reaction mechanisms,3,4) control of ion transport,5,6) etc.7) The essential idea that is common among these investigations seems to be related to unique characters of liquid crystals such as molecular orientation and phase transition. If these properties are controlled by chemical and physical signals, this leads to the control of various events occurring in liquid crystal media. Recently, we synthesized new steroidal crown compounds (**1** and **2**).8,9) We found that when alkali metal cations are added to a mixture of cholesterol nonanoate (ChN) and cholesterol chloride (ChC) (a room temperature liquid crystal) containing **1**, a helical pitch of the mixed cholesteric liquid crystals is changed.10) The magnitude of the pitch change is basically explained by the spherical recognition pattern frequently observed for crown-metal interactions.10) On the other hand, compound **2** having an ethylene spacer between the crown and the cholesterol moiety induced no pitch change. Also interesting is the finding that the helical pitch is changed by the size of counteranions. These results tempted us to test if the system is capable of discrimination of optically-active counteranions through an enantioselective interaction: the pitch (i.e., color) may change differently between (R)- and (S)-counteranions. Here, we newly synthesized **3** having a monobenzo-13-crown-4 moiety11) and examined chiral recognition of alkali (R)- and (S)-mandelates as guest molecules by **1**-**3**.

ChN (1.2×10^{-5} mol), ChC (0.8×10^{-5} mol), steroidal crown (**1**, **2**, **3**,



1a:n=1
1b:n=2



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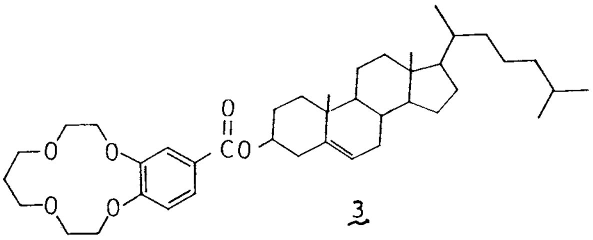

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or 4'-methoxycarbonylmonobenzo-18-crown-6(4) used as a reference compound: 0.9×10^{-5} mol), and alkali mandelate were dissolved in chloroform (1.0 ml). An aliquot (about 0.2 ml) of this solution was spread on a glass plate and mixed with minute glass beads with the uniform diameter (10 ± 0.2 μm). The wavelength of maximun reflection (λ_R = nP, where n is the mean index of reflection and P is the helical pitch of the cholesteric mesophase) was measured spectrophotometrically at 27 °C.[12)]

Figure 1 shows plots of λ_R vs. [potassium mandelate]/[1b] in the ChN-ChC-1b system. It is seen from this figure that with increasing mandelate concentration, the λ_R for (R)-isomer efficiently increases whereas that for (S)-isomer increases only slightly. The λ_R difference at [potassium mandelate]/[1b] = 0.08 amounts to 61 nm. The color difference (green for (R)-isomer and blue for (S)-isomer) could be visually differentiated. In contrast, potassium mandelate scarcely changed the λ_R in the ChN-ChC-4 system (data not shown: see Table 1). When sodium mandelate was added to ChN-ChC-1b instead of potassium mandelate, the difference in the λ_R between the two optical isomers was scarcely recognized (Fig. 2). We also confirmed that the addition of tetrabutylammonium mandelate, which does not interact with the crown ring, scarcely changes the helical pitch.

We measured the λ_R shifts for several alkali and NBu_4^+ mandelates at [mandelate]/[steroidal crown] = 0.08. The results are summarized in Table 1. Examination of Table 1 reveals that (i) when the metal cation fits the size of the crown ring, the large λ_R difference between (R)- and (S)-isomers was induced (as in 1a-Na^+ and 1b-K^+), (ii) the λ_R difference was observed to a smaller extent for ChN-ChC-2 and scarcely for ChN-ChC-4, (iii) the λ_R difference induced by Li^+ is generally smaller than those induced by Na^+ or K^+ but becomes greater only in ChN-ChC-3, and (iv) generally, the λ_R values for (R)-isomer appear at longer wavelengths than those for (S)-isomer. These findings consistently support that the inter-

Table 1. Shift (nm) of λ_R induced by added alkali and Bu_4N^+ mandelates[a)]

Liquid crystal	Chirality of mandelates	λ_R[b)]	Mandelate salt			
			$M^+ = Li^+$	Na^+	K^+	Bu_4N^+
ChN-ChC-**1a**	(R)	455	15 ± 2	61 ± 3	63 ± 4	
	(S)		-11 ± 2	-1 ± 2	38 ± 2	
ChN-ChC-**1b**	(R)	455	13 ± 3	37 ± 1	69 ± 5	-1 ± 7
	(S)		5 ± 6	35 ± 3	8 ± 3	-2 ± 7
ChN-ChC-**2**	(R)	825	-4 ± 6	20 ± 11	-13 ± 4	
	(S)		-24 ± 2	-2 ± 4	-33 ± 4	
ChN-ChC-**3**	(R)	790	-4 ± 4	-2 ± 5	-19 ± 9	
	(S)		-15 ± 6	-2 ± 7	-18 ± 6	
ChN-ChC-**4**	(R)	670	6 ± 2	3 ± 3	11 ± 2	
	(S)		5 ± 3	1 ± 4	9 ± 3	

a) [Mandelate]/[steroidal crown] = 0.08. The λ_R values are the average of four repeated runs.

b) The λ_R values in the absence of mandelates salts.

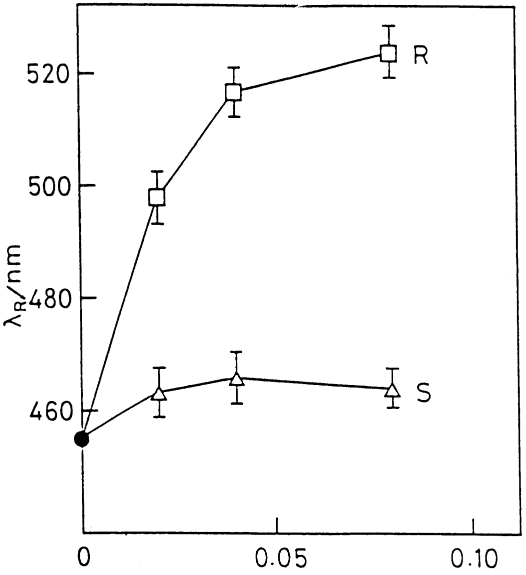

Fig. 1. Plots of λ_R vs. [K^+ mandelate]/[**1b**] in ChN-ChC-**1b**. The λ_R values are the average of four repeated runs. The error range is shown by bars.

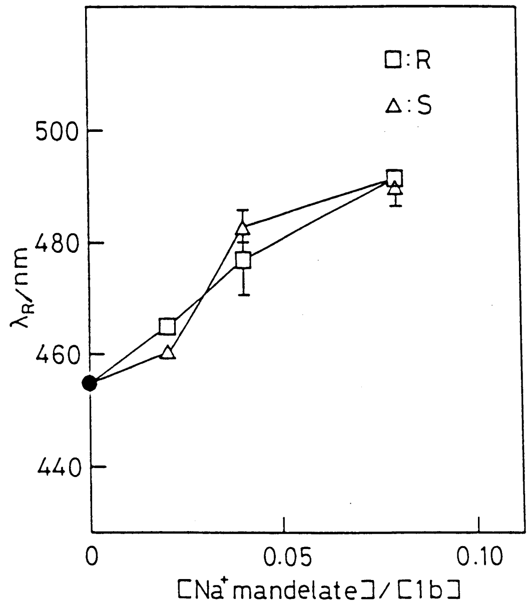

Fig. 2. Plots of λ_R vs. [Na^+ mandelate]/[**1b**] in ChN-ChC-**1b**.

action between the additive and the crown ring and the "direct" covalent-linkage between the cholesterol moiety and the crown ring are primarily essential to the effective λ_R change. Conceivably, the complexation event occurring in the ion-binding site is efficiently transmitted to the structure-forming cholesterol moiety only when these prerequisites are satisfied.

In conclusion, the present paper demonstrated that chiral alkali mandelates bound to the crown ring in cholesteric liquid crystals change the helical pitch in an enantioselective manner, which can be detected by the difference in the color change. These results suggest that the present liquid crystal system serves as a new chiral sensory system.

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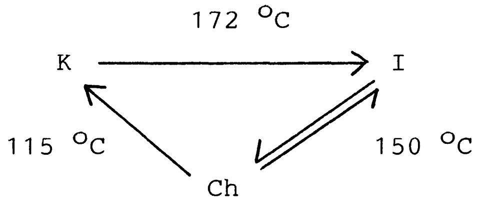
11)Compound **3** was synthesized from cholesterol and 4'-carboxymonobenzo-13-crown-4 in a method similar to that used for the synthesis of **1**[8]: yield 26%. This compound showed the following phase diagram.



12)For the measurement method, see P. J. Shannon, Macromolecules, **17**, 1873(1984).

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