Crown–Metal Interactions in Cholesteric Liquid Crystals

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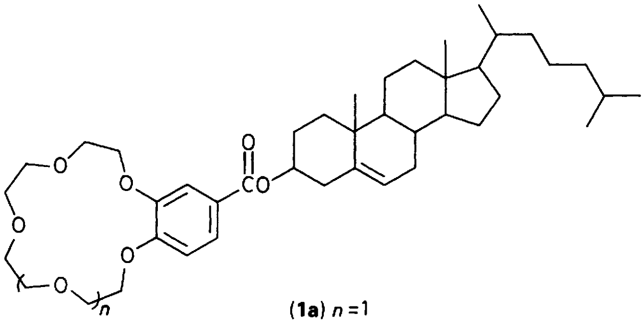
Alkali metal cations bound to steroidal crown ethers can change the helical pitch of cholesteric liquid crystals; the results indicate a potential to apply the liquid crystal as a new host–guest sensory system.

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 seems to be common among these investigations is 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 synthesised new steroidal crown compounds (**1**) and (**2**).[8,9] Alkali metal cations permeate through the thin membranes composed of these steroidal crown compounds and the ion selectivity based on the crown ether rings is observed.[9,10] We were interested in how the steroidal crown compounds interact with alkali metal cations in the liquid crystal media and what influence the bound metal cations exert on the liquid crystalline structure. We report here the influence of the bound alkali metal cations on the helical pitch of a cholesteric liquid crystal. We have found that the helical pitch is sensitively affected not only by the bound metal cations, but also by the counteranions. The results suggest a potential to apply this liquid crystal as a new host–guest sensory system.

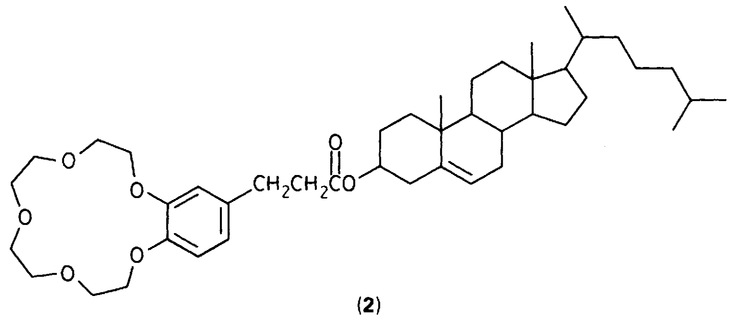
Preparations of (**1**) and (**2**) were described previously.[8,9] A mixture of cholesterol nonanoate (**3**) and cholesterol chloride (**4**) is known as a room temperature liquid crystal. Compound (**3**) (1.2×10^{-5} mol), (**4**) (0.8×10^{-5} mol), (**1**) or (**2**) (0.6×10^{-5} mol), and MSCN (M = alkali metal cation) were dissolved in chloroform (1.0 ml). An aliquot (usually 200 µl) of this solution was spread on a glass plate and mixed with minute glass beads with the uniform diameter (10 ± 0.2 µm). The solution was dried and sandwiched with another glass plate. The thickness of the sample thus prepared is regulated by the glass beads. The wavelength of maximum reflection ($\lambda_R = nP$, where n is the mean index of reflection and P is the helical pitch of the cholesteric mesophase) was measured spectrophotometrically at 27 °C.[11]

Figures 1—3 show plots of λ_R *vs.* [MSCN]/[(**1**) or (**2**)]. The relative error for repeat measurements of λ_R was less than 4%. As shown by plots on the ordinate in these figures, the λ_R changes upon addition of (**1**) or (**2**): the shifts from the λ_R in the absence of these steroidal crown compounds (674 nm) are −223 nm for (**1a**), −219 nm for (**1b**), and +74 nm for (**2**). The finding indicates that the helical structure of a (**3**)–(**4**) mixed cholesteric liquid crystal is widened by (**2**) but narrowed by (**1a**) and (**1b**). It is seen from Figures 1 and 2 that the λ_R changes sensitively in response to the type and the concentration of M^+. The largest shift is attained in the presence of K^+ for (**1a**) and Cs^+ for (**1b**). In particular, the shift attained in K^+–(**1a**) at [KSCN]/[(**1a**)] = 0.10 amounts to +46 nm (the colour change can be visually detected).

In contrast, the λ_R for (**2**) was scarcely affected by the addition of these metal cations (Figure 3). We also used 4′-methoxycarbonylmonobenzo-18-crown-6 instead of (**1**) or (**2**): the result was similar to Figure 3. The findings provide an important clue to explain why the λ_R for the (**1**)–(**3**)–(**4**) ternary system changes upon addition of metal cations. Since MSCN is scarcely soluble in the (**3**)–(**4**) mixed medium, it should be solubilised through the complexation with the crown ether moiety. If the metal-binding crown site is directly linked to the structure-forming cholesteric site [such as (**1**)], the event occurring at the metal-binding site is transduced to



(**1a**) $n = 1$
(**1b**) $n = 2$



(**2**)

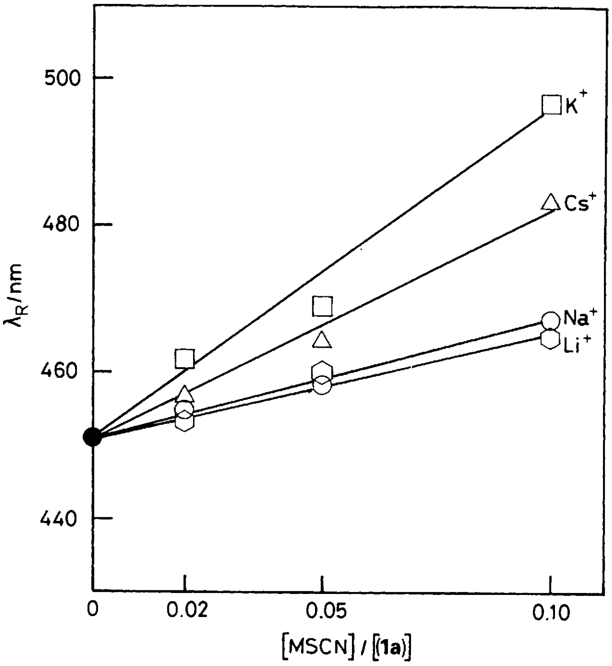


Figure 1. Plots of λ_R *vs.* [MSCN]/[(**1a**)].

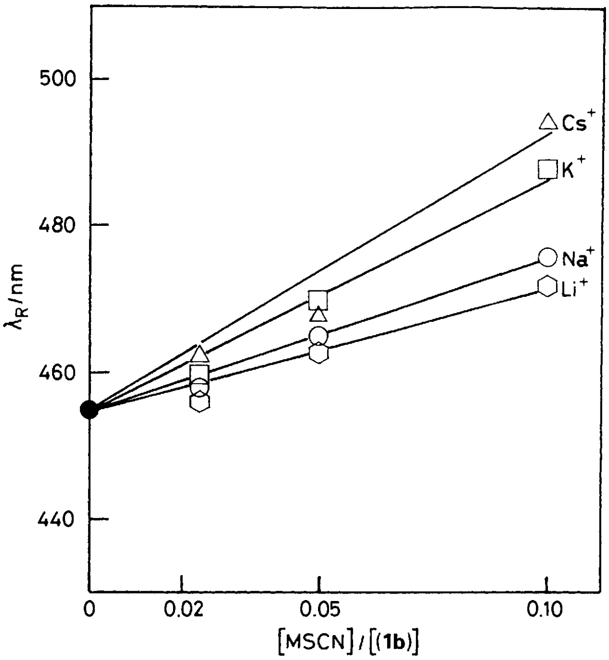


Figure 2. Plots of λ_R *vs.* [MSCN]/[(**1b**)].

the cholesteric site and changes the helical pitch. However, if a spacer is inserted between the two sites [such as (**2**)], the event occurring at the metal-binding site is absorbed by the flexible molecular segment in the spacer.

We also found that the λ_R can be changed by the size of conteranions (X^-). In the (**1b**)–(**3**)–(**4**) system, for example, the λ_R values for KX at [KX]/[(**1b**)] = 0.10 are 474 nm for Cl^-, 507 nm for ClO_4^-, 487 nm for SCN^-, and 537 nm for tetrakis(*p*-chlorophenyl)borate. Evidently, the helical pitch increases with the increase in the size of X^-.

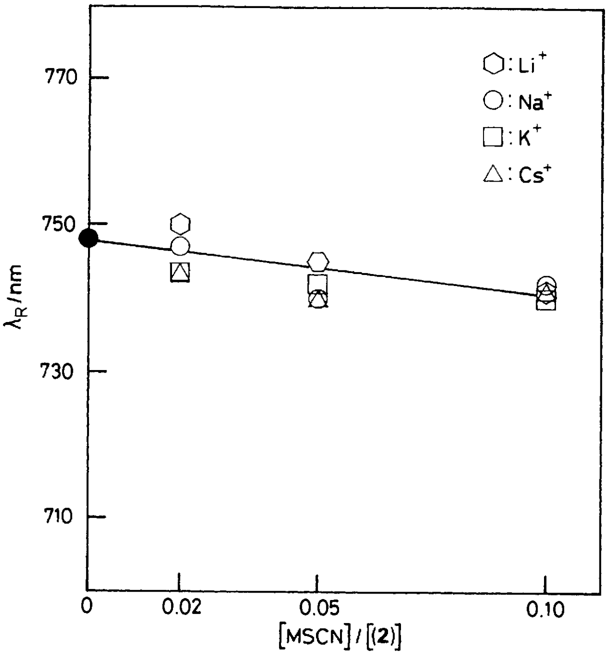


Figure 3. Plots of λ_R *vs.* [MSCN]/[(**2**)].

The foregoing results indicate that alkali metal salts bound to the crown rings in (**1**) change the helical pitch, which can be detected spectroscopically. Thus, this system is regarded as a novel transformation of chemical signals to physical signals. Of particular interest among future plans is the idea to test if the system can 'recognise' optically-active guest molecules through a diastereoisomeric interaction. A preliminary experiment using (*R*)- and (*S*)-1-phenylethylalanine methyl ester hydrochloride as guest molecules shows that the helical pitch in the (**1b**)–(**3**)–(**4**) system is different between these enantiomers. These findings consistently suggest that the present system acts as a new, promising host–guest sensory system.

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