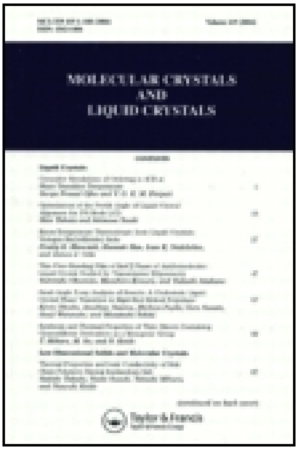

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Mesomorphism of Cholesteryl Halopropionate

Shinichi Yano [a] , Yoshiyuki Nabata [a] & Koichiro Aoki [a]
[a] Department of Synthetic Chemistry, Gifu University, Kagamigahara, Gifu, 504, Japan

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Mesomorphism of Cholesteryl Halopropionate†

SHINICHI YANO, YOSHIYUKI NABATA and KOICHIRO AOKI

Department of Synthetic Chemistry, Gifu University, Kagamigahara, Gifu 504, Japan

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Mesomorphisms of several cholesteryl monohalopropionates have been studied. The β-monohalopropionates exhibited a cholesteric liquid crystal phase, but the α-monohalopropionates had no mesophase. These results were explained by the lateral dimensions of rigid lathlike cholesteryl compounds.

INTRODUCTION

Mesomorphisms of cholesteryl *n*-alkanoates have been extensively studied by many workers,[1-4] because most of them exhibit the typical cholesteric liquid crystal state. However, mesomorphic properties of cholesteryl halopropionates have not been paid much attention, and to our knowledge, this seems to arise from the presumption that the mesomorphisms of cholesteryl haloalkanoates would take after those of the alkanoates. The present investigation has aimed at elucidating the influence of halogen atom on the existence of mesomorphic state in cholesteryl halopropionate. The cholesteryl halopropionates used here are α-chloropropionate, β-chloropropionate, α-bromopropionate, β-bromopropionate, and 2,2,3,3,-tetrafluoropropionate.

EXPERIMENTAL

The cholesteryl halopropionates were synthesized by refluxing ligroin solution of cholesterol, halopropionic acid, and small amount of *p*-toluene sulfonic acid in a flask with the Dean Stark tube.[3] The solution containing the product was washed thoroughly with 20% ethanol and dried with anhydrous

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sodium sulfate. The crude sample was crystallized from the solution by cooling it at about 0 °C. After washing the sample with ligroin, the sample was purified by recrystallizing it alternately from acetone and ligroin solution. The samples obtained were identified to be thoroughly purified by IR, NMR, thin layer chromatograph and DSC. In particular, it is emphasized that cholesteryl esters with a very low electrical conductivity were obtained by this synthetic method.[2,3] (see Figure 1.)

Phase transitions were measured by a DSC (Perkin Elmer, DSC IB) calibrated with galium and indium, and by a polarized light microscope with a hot stage, at a heating rate of about 10 °C/min. Dielectric measurements were carried out with a transformer bridge in the way described previously.[5]

RESULTS AND DISCUSSION

Phase transition of cholesteryl halopropionate

Phase transition temperatures, and transition enthalpies, ΔH, and entropies, ΔS, of various samples are listed in Table I. Cholesteryl propionate exhibits the cholesteric phase at temperatures between 95.6 and 110.9 °C, being fairly well consistent with those by many workers.[1-4] In cholesteryl monohalopropionates, the β-halopropionates exhibit a cholesteric phase as well as cholesteryl propionate, while the α-halopropionates have no mesophase. These interesting phenomena seem to be related to the lateral dimensions in the rigid lathlike molecule of cholesteryl derivatives. Namely, the absence of meso-

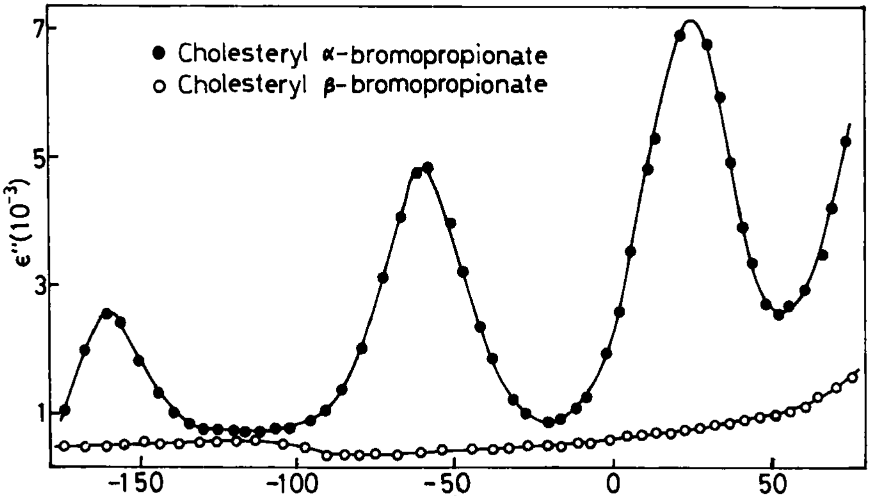

FIGURE 1 Temperature dependences of dielectric loss, ϵ'', in the crystalline phase of cholesteryl α- and β-bromopropionate at 10 kHz.

TABLE I

Phase transition parameters for cholesteryl halopropionates

Sample	Transition temperature °C	Enthalpy of transition $\Delta H_{\mathrm{C-Ch}}$ kJ/mole	$\Delta H_{\mathrm{Ch-I}}$ kJ/mole	$\Delta H_{\mathrm{C-I}}$ kJ/mole	Entropy of transition $\Delta S_{\mathrm{C-Ch}}$ J/mole·deg	$\Delta S_{\mathrm{Ch-I}}$ J/mole·deg	$\Delta S_{\mathrm{C-I}}$ J/mole·deg
Cholesteryl propionate	$\mathrm{C} \underset{86.3}{\overset{95.6}{\rightleftharpoons}} \mathrm{Ch} \underset{110.0}{\overset{110.9}{\rightleftharpoons}} \mathrm{I}$	22.7	0.25		61.6	0.6	
Cholesteryl α-methylpropionate	$\mathrm{C} \underset{115.3}{\overset{127.5}{\rightleftharpoons}} \mathrm{I}$			25.2			62.9
Cholesteryl α-chloropropionate	$\mathrm{C} \underset{105.0}{\overset{135.9}{\rightleftharpoons}} \mathrm{I}$			48.5			119
Cholesteryl β-chloropropionate	$\mathrm{C} \underset{64.5}{\overset{86.7}{\rightleftharpoons}} \mathrm{Ch} \underset{122.0}{\overset{124.8}{\rightleftharpoons}} \mathrm{I}$	19.9	0.74		55.3	1.9	
Cholesteryl α-bromopropionate	$\mathrm{C} \underset{97.9}{\overset{136.3}{\rightleftharpoons}} \mathrm{I}$			35.7			87.2
Cholesteryl β-bromopropionate	$\mathrm{C} \underset{77.7}{\overset{101.8}{\rightleftharpoons}} \mathrm{Ch} \underset{115.5}{\overset{116.8}{\rightleftharpoons}} \mathrm{I}$	20.8	0.49		55.5	1.2	
Cholesteryl 2,2,3,3-tetrafluoropropionate	$\mathrm{C} \underset{132.2}{\overset{149.4}{\rightleftharpoons}} \mathrm{I}$			28.6			67.7

* C: Crystal phase, Ch: Cholesteric phase, I: Isotropic phase

phase in the α-halopropionates may be understood by the increase of lateral dimensions with the halogen atom, because cholesteryl α-methylpropionate has also no mesophase.

The β-monohalopropionates have the cholesteric liquid crystal phase, as described above. The clearing temperature, T_c, of the β-monochloropropionate is higher than that of the propionate. This can be explained by an increase of interaction between end groups by the substitution of H atome with Cl atom in the β-position of the propionate. While the value of T_c in the β-bromopropionate is lower than that of the β-chloropropionate, and this may be caused by the increase of lateral dimensions. Consequently, the thermal stability for cholesteric phase in cholesteryl β-monohalopropionates can be explained by both the intermolecular interaction in the cholesteric phase and the lateral dimensions of rigid lathlike molecule, as indicated generally in mesomorphic compounds.[6] Barallel-Bredfeldt-Vogel's results[7] on phase transitions of cholesteryl monohalobenzoates and monohalocinnamate are similar to our results in this paper. They indicated that the transition temperatures are sensitive to the substituent location in a benzene ring and that the effect of the location on the temperature can be explained by steric factor of ester group and intermolecular interaction.

It is reported by Murza-Bil'dinov-Shcherbakova[8] that cholesteryl perfluoropropionate had monotropically a cholesteric phase between 76 and 79 °C on the cooling process. However, cholesteryl 2,2,3,3,-tetrafluoropropionate does not exhibit any mesophase. This is interesting but the interpretation may be performed by further studies, because Barallel, Johnson and Porter[9] assert that cholesteryl perfluorobutylate which is purified very carefully has no mesophase, whereas Murza *et al.*[7] observed a cholesteric mesophase on cooling.

Dielectric relaxations in the crystalline phase of cholesteryl α- and β-bromopropionates

Figure 1 shows temperature dependence of dielectric loss, ε″, in the crystalline phase of cholesteryl α- and β-bromopropionate at 10 kHz. Clearly, there are three relaxations near −160, −60 and 25 °C (named I-, II- and III-relaxations, respectively) in the α-bromopropionates, whereas in the β-bromopropionate, any relaxation can not be observed in the temperature range of −180 to 70 °C. The Arrhenius plots for the three relaxations are shown in Figure 2. The values of the activation enthalpies, Δ*H*, and the entropies, Δ*S*, calculated from the slopes are listed in Table II. The values of Δ*H* become larger from I-to III-relaxation in order. This suggests that three relaxations are related to three distinct rotational motions of α-bromopropionyloxy group. The internal rotational motion of propionyloxy group may be much hindered by Br atom at α-position and would appear as the three distinct relaxations in the crystalline state. On the other hand, it is of interest that the β-bromopropio-

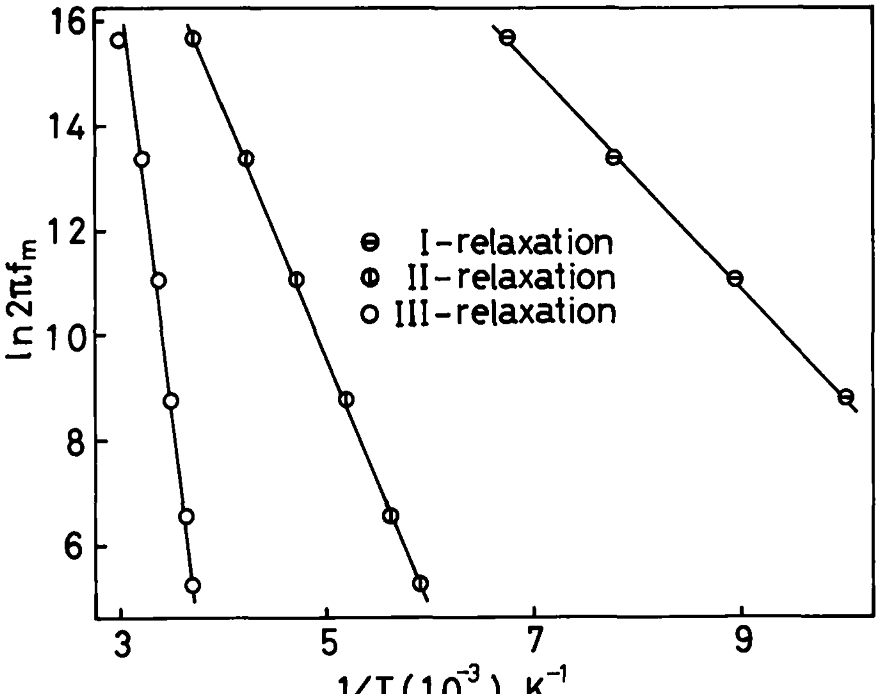

FIGURE 2 The Arrhenius plots of three relaxations in the crystalline phase of cholesteryl α-bromopropionate.

nate has no relaxation in the crystalline state. This can be understood by a presumption that the Br atom at β-position would not affect so much rotationary motion of propionyloxy group.

In conclusion, the dielectric relaxation behavior which may reflect molecular structure and crystal structure seems to be associated with the characteristic mesomorphism of cholesteryl monohalopropionates.

TABLE II

Relaxation parameters for three relaxations in the crystalline phase of cholesteryl α-bromopropionate.

Relaxation	Relaxation temperature at 10 kHz K	ΔH kJ/mole	ΔS J/mole·deg
III	298	139	310
II	213	37	23
I	112	16	−0.8

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