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Optical and thermal properties of cholesteric solid from dicholesteryl esters of diacetylenedicarboxylic acid

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Dicholesteryl esters of diacetylenedicarboxylic acid with different lengths of methylene linkages were synthesised. Compounds with $(CH_2)_n$ ($n=2$, 4, 5, 6, 7, 8, 10) showed a cholesteric phase. Phase transition temperatures from the isotropic phase to the anisotropic phase showed an odd–even effect of the number of (CH_2) units. By rapid cooling from the cholesteric phase to 0 °C, the compounds were solidified retaining the cholesteric colours (cholesteric solid), some of which were stable at room temperature. Changing the temperature at which rapid cooling started changed the colours of the cholesteric solid. The thermal stability of the cholesteric solid also showed an odd–even effect of the number of (CH_2) units. The effect can be explained by the difference in the stable structures of the molecules and the strength of the weak intermolecular interactions *via* carbonyl groups between the compounds with odd and even (CH_2), which was observed in the FT-IR spectra.

Introduction

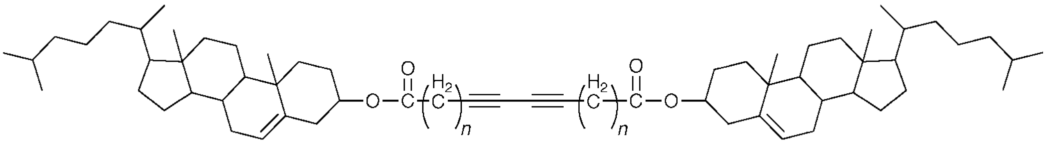
Although one sees many studies on liquid crystalline compounds (LC) with low molecular weights (less than about 1000) and no molecular weight distributions or with high molecular weight (over 10 000) typically with molecular weight distributions, the number of studies that focus on the synthesis and properties of LCs with medium molecular weight is limited.[1,2] One can expect not only intermediate properties for the LCs with medium molecular weight but also unique properties lacking in LCs with low or high molecular weight. Recently, we observed that a symmetric dicholesteryl ester of a diacetylenedicarboxylic acid with eight methylene units connecting the cholesteryl and diacetylene units on each wing (molecular weight is 1099.8) (**1–8**) formed solids that exhibit fixed cholesteric colours due to cholesteric molecular ordering.[3] The preparation of these solid states was accomplished by rapid cooling from a cholesteric phase to 0 °C or even room temperature. By changing the temperature at which rapid cooling starts within the cholesteric temperature range, we could fix the colours chosen from any visible region such as blue, green and red.[4] The coloured solid states are totally stable up to about 70 °C, however, they change into a crystalline state once heated to 80 °C and melted at 120 °C. The response time of a molecular re-alignment at cholesteric temperature is reasonably low as in LCs with low molecular weight, and the solid state with cholesteric molecular ordering is quite stable as in LCs with high molecular weight. The compound can therefore be considered as one of the candidates for rewritable full-colour recording media.[5,6]

To see the effect of the molecular weight and the length of the flexible units on the thermal and optical properties of cholesteric solids, we have synthesised a series of symmetric dicholesteryl esters of diacetylene dicarboxylic acids with different numbers of methylene units, **1–*n*** ($n=2$, 3, 4, 5, 6, 7, 8, and 10). Some results are known for the linear and odd–even effects of the length of the alkylene linkages in similar dicholesteryl esters without a diacetylene unit on the phase transitions between isotropic and cholesteric or cholesteric and crystalline phases.[7–9] However, no studies to date have been concerned with the properties of the cholesteric solids. In this paper, we report the liquid crystalline properties of the newly synthesised dicholesteryl esters and thermal and optical properties of the cholesteric solids of the compounds, especially from the viewpoint of the even–odd effect of the methylene units connecting the cholesteryl and diacetylene units. Furthermore, we discuss the driving force that stabilises the cholesteric-like molecular ordering in the solid phase based on the results of infrared absorption measurements.

Results and discussion

Phase transitions

The dicholesteryl esters **1–*n*** ($n=2$, 4, 6, 8, and 10) exhibited monotropic phase transitions. They did not show any liquid crystalline phases on heating but showed two transitions, between which the cholesteric colours were observed, on cooling. **1–3** did not show any mesophases even on cooling. **1–5** did not show a mesophase on cooling at a 2 °C min^{-1} cooling rate, but a blue cholesteric colour was seen when the compound was rapidly cooled from the isotropic phase to around 70 °C. This unusual cholesteric phase was metastable and crystallised when kept at 70 °C for a long time. A similar phenomenon has already been reported for the cholesteryl formate.[10] **1–7** showed two exotherms, between which choles-



1-*n* ($n = 2$, 3, 4, 5, 6, 7, 8, 10)

Structure of molecules.

Table 1 Phase transition temperatures of **1–*n*** on cooling measured by DSC in °C; corresponding enthalpy change in mJ mol^{-1} in parentheses

Compound	Iso.→Chol. or Cryst.	Chol.→Cryst.	Chol.→Sm.	Sm.→glass
1–2	222[a]	192 (−21.1)		
1–3	122 (−20.2)			
1–4	163 (−3)	132 (−22.8)		
1–5	106 (−23.1)			
1–6	131 (−2.1)	91 (−25.2)		
1–7	103 (−1.0)		85 (−0.47)	13
1–8	117 (−1.7)	82 (−14)		
1–10	105 (−2.1)	80 (−15.4)		

[a]Temperature read from polarising microscope measurement.

teric colours were observed, and a second order transition below the exotherms on cooling. Fig. 1 shows the DSC curve for **1–6** that is representative of the dicholesteryl compounds with monotropic phase transitions. One can see the difference in the temperature between the transitions from crystal to isotropic on heating and from isotropic to cholesteric on cooling. Transition temperatures and the exothermic heat on cooling measured by DSC for **1–*n*** are summarised in Table 1. Fig. 2 shows the phase transition temperatures measured by DSC plotted against the number of methylene units in each flexible linkage. Generally, phase transition temperatures shifted toward lower temperatures with an increasing number of methylene units. Furthermore, it was apparent that the even–odd effect of the methylene units affected the phase transition temperature from isotropic phase to anisotropic phases. The cholesteric phase was stabilised by the introduction of an even number of methylene units or by increasing the length in the case of an odd number of methylene units. Marcelis *et al.* reported a similar odd–even effect of the number of atoms that connect two or three mesogenic units on the phase transitions of cholesteric liquid crystals.[8,9] According to their explanations, if the number of the connecting atoms is even and an all-*trans* like configuration is assumed, the linked mesogens align parallel to each other. The parallel formation should stabilise the liquid crystalline phase. In the case where the mesogens are connected with an odd number of atoms, the mesogens form an angle smaller than 180°, which destabilises the liquid crystalline phase. In the case of the dicholesteryl esters of diacetylenedicarboxylic acid used in this study, one of the interesting questions is whether or not the diacetylene unit functions as a mesogen. If the diacetylene unit does not function like a mesogen but just as a long straight linkage, the molecules can be recognised as diad-type, and all compounds with any number of methylenes are considered to have even atoms in the linkage. However, we observed a clear even–odd effect. This means that the diacetylene unit serves like a mesogen in this case and the molecules can be considered as triad-types.

Cholesteric solid state

The compounds **1–*n*** ($n=2$, 4, 5, 6, 7, 8, and 10) showing a cholesteric phase were solidified by rapid cooling from the cholesteric phase to 0 °C, retaining the cholesteric colours. Fig. 3 shows the transmission spectra of **1–6** in the coloured solid state sandwiched between a pair of thin glass plates. Selective reflection bands, which are one of the typical features of cholesteric liquid crystalline compounds, were observed for the solid film of **1–6**. The peak of the band shifted from 393 to 693 nm on changing the temperature at which rapid cooling starts in the cholesteric phase, from 130 to 72 °C, respectively. A cholesteric phase of **1–6** below 91 °C (cholesteric–crystal transition) was obtained as a supercooled state by transferring the compound from a hot stage at 140 °C to another stage below 91 °C. About 50% of the light was reflected for each film at the peak. A large optical rotatory dispersion, up to 15° μm^{-1} in the positive sense, was also observed around the peak of the reflection band for the solid film from **1–8**.[11] All of these observations verify that the molecules aligned in cholesteric-like ordering in the coloured solid state.

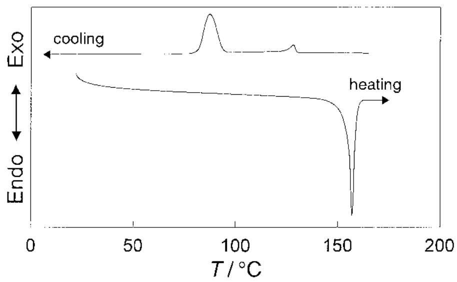


Fig. 1 DSC thermogram of **1–6** on second heating and second cooling.

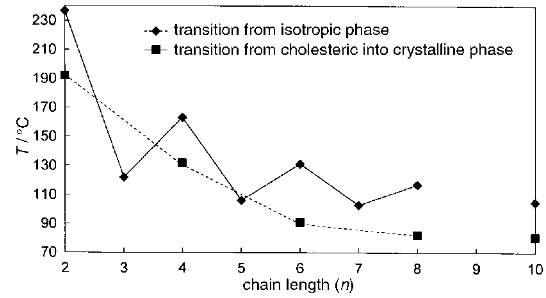


Fig. 2 Phase transition temperatures of **1–*n*** measured by DSC on cooling plotted against the number of methylene units in each flexible linkage. The transition temperature of **1–2** from the isotropic phase to the cholesteric phase was measured under a polarised microscope because of its instability at high temperature. **1–3** and **1–5** crystallised directly from isotropic phases on cooling at 2 °C min^{-1}. **1–7** did not crystallise but changed into a glassy state *via* a smectic phase.

The ease of fixing the cholesteric colours, the region of the fixed reflection bands and the thermal stability of the cholesteric solid states were highly dependent on the length of the methylene units in the molecules as summarised in Table 2. **1–2** and **1–4** showed mainly a blue colour over a wide spectral region in the cholesteric phase, and the colour was not

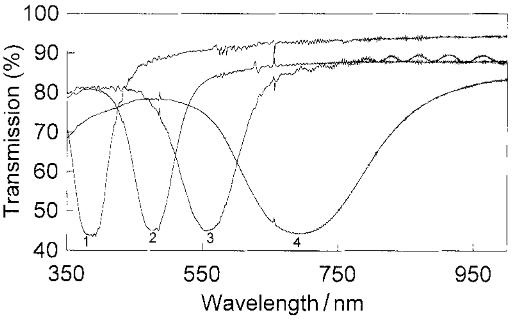


Fig. 3 Transmission spectra of **1–6** in the coloured solid state sandwiched between a pair of thin glass plates obtained by cooling from different temperatures. 1: 130 °C, 2: 90 °C, 3: 75 °C, 4: 72 °C.

Table 2 Molecular weight of **1–*n*** and the properties of the cholesteric solid state

Compound	M_w	Ease of fixing colour/°C[a]	Range of fixed colours	Crystallisation temp./°C[b]
1–2	931	0	Blue	166
1–3	959	—	—	—
1–4	987	0	Blue	116
1–5	1015	25	Blue, green, red	16
1–6	1043	25	Blue, green, red	40
1–7	1071	25	Blue	18
1–8	1099	25	Blue, green, red	80
1–10	1155	25	Blue, green, red	23

[a] The temperature to which the system was cooled to obtain the cholesteric solid. [b] This temperature is the transition temperature from the cholesteric solid to the crystalline state observed on a hot stage.

sensitive to a change in the temperature in the cholesteric LC region. Only the blue colour was fixed in the solid state with those compounds by rapid cooling from the cholesteric temperature to 0 °C. The compounds with longer alkylene chains, **1–*n*** (*n* = 5, 6, 7, 8 and 10) showed various colours from blue to red depending on the temperature, which could be fixed in the solid state by rapid cooling from the cholesteric temperature to 0 °C or even to 25 °C, the latter procedure of which serves as a slower cooling.

The fixed colours of **1–2**, **1–4** and **1–8** were stable at room temperature, however, the colours for the other compounds were rather unstable. **1–5** and **1–7**, which contain an odd number of methylene units in each wing, were particularly unstable. The stability seems to be almost independent of the fixed colours. Upon heating, the coloured solid films of **1–*n*** changed into white crystals at a certain temperature that depends on the compound. Fig. 4 shows the DSC thermogram for **1–6** from the coloured solid state, which shows exotherms for the phase transition from the cholesteric solid to the crystalline state and the endotherm for the transition from the crystalline state to the isotropic phase at 40 and 155 °C, respectively. More careful observation reveals that a second-order-like transition appears just before the transition from the cholesteric solid to the crystalline state. Under observation on a temperature-controlled hot stage, the state between the second-order-like transition and the crystallisation from the cholesteric solid was sticky. These observations lead us to the conclusion that the second-order-like transition is the glass transition temperature. For **1–8**, a glass transition temperature was similarly seen, but not for the other compounds. Fig. 5 shows the DSC thermograms from the coloured solid states (blue, green and red) for **1–8**. We see the glass transition temperatures and crystallisation temperatures from the cholesteric solid states around 78 and 85 °C, respectively. These transition temperatures are much higher than those for **1–6**. Another interesting feature, which was apparent for **1–8**, is that two kinds of exothermic peaks for melting points existed at 117 and 119 °C and that the ratio of the heat for the two peaks changed depending on the fixed colour at the solid state. As the colour shifted toward a shorter wavelength, the ratio of the heat at 117 °C increased. With the optical microscope on the hot stage, no mesophase but only white crystals below 117 °C were observed on heating from the blue cholesteric solid phase. Thus these peaks were identified as heats of melting of the two kinds of crystals for **1–8** with different molecular ordering.

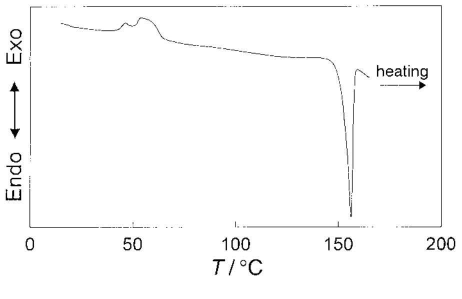


Fig. 4 DSC thermogram of **1–6** on heating from the blue solid state.

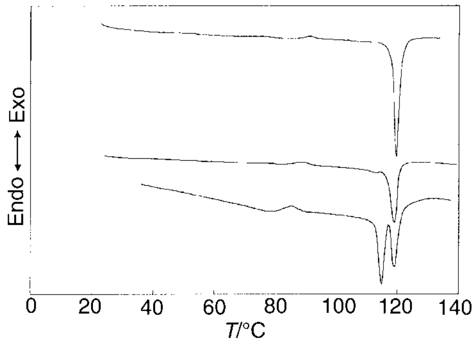


Fig. 5 DSC thermograms of **1–8** on heating from the blue, green and red solid states. Top, from red solid state; middle, from green solid state; bottom, from blue solid state.

Infrared spectra

In order to find the origin of the interactions between molecules which stabilise the cholesteric solid structure, the infrared spectra of the cholesteric solid and crystalline state were compared for each **1–*n***. Generally, shifts in the wavenumber for peaks from the crystalline state to the cholesteric solid state were very small for any **1–*n***. Only the carbonyl stretching that appears around 1730 cm^{-1} shifted regularly from the crystalline state to the cholesteric solid. Fig. 6 shows the wavenumber for carbonyl stretching plotted against the number of methylenes in each wing of the dicholesteryl esters. An odd–even effect on the wavenumber is clearly seen, which means that the crystalline state showed higher wavenumbers for the carbonyl stretching than for the cholesteric solid states for the compounds with an even number of methylenes, while the opposite tendency was seen for the compounds with an odd number of methylenes. Among the compounds with an even number of methylenes, the difference in the wavenumber for **1–10**, which showed the lowest stability, was the smallest.

It is known that the wavenumber of the carbonyl stretching depends on the electronic structures.[12] The contribution of the dipolar structure (b) in Fig. 7, which has the character of a single bond in the carbonyl C–O linkage, reduces the wavenumber of the carbonyl stretching.[12b] For simple esters, the vapours show a higher wavenumber of the carbonyl stretching than the condensed liquids that are composed of a dimeric form of the molecules in the dipolar structure. The information on the effect of the contribution of the dipolar electronic structure on the reduction of the wavenumber of carbonyl stretching allows us to conclude that carbonyl groups in the molecules with even methylene linkages exist as more dipolar electronic structures in the cholesteric solid than in the crystalline state. For the molecules with odd methylene linkages, the opposite can be concluded. The dipolar structures will induce an intermolecular dipole–dipole interaction that

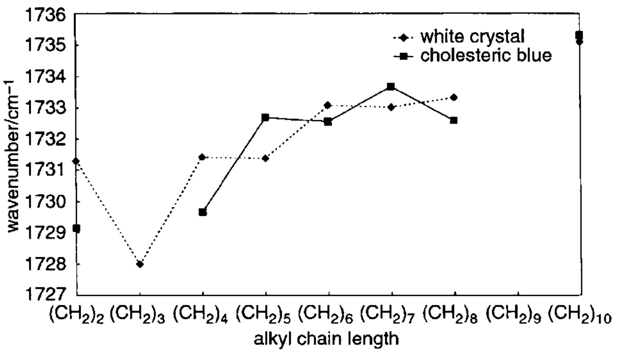


Fig. 6 Vibrational frequency of carbonyl linkages in **1–*n*** in the crystalline state (◆) and blue cholesteric solid state (■) plotted against the number of methylene units in each flexible linkage. **1–3** did not show a cholesteric phase.

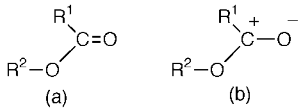


Fig. 7 Electronic structures of compounds containing a carbonyl group. The proportion of (b) is increased by condensation from vapour to liquid, because dipolar association occurs in the liquid state. This change in the electronic structure is observed as a decrease in vibration frequency of a carbonyl linkage.[12b]

serves as the driving force to form a linear polymeric structure in the case of the molecules with two carbonyl groups.

The reason why the intermolecular distances between carbonyl groups are changed depending on the even or odd number of methylenes is apparent if we consider the structures of the molecules with odd and even methylenes assuming the all-*trans* alkylene conformation. The molecule with even methylenes has a linear structure, while the molecule with odd methylenes has a zigzag structure. Molecules should rotate around the long axis of the molecule in a cholesteric phase, so the excluded volume around the carbonyl group for the molecule with odd methylenes is larger than that of the molecule with even methylenes.

Conclusions

The present study involved highly stable cholesteric solid states of medium molecular weight compounds. Dicholesteryl esters with molecular weights higher than 1000 and containing a diacetylene unit in the flexible chain showed slower crystallisation and formed a cholesteric solid without any difficulty by cooling from the cholesteric temperature to 0 °C. The colours of the cholesteric solid were changed by changing the temperature at which rapid cooling started. The high thermal stability of the cholesteric solid can be explained by the formation of the polymer-like structure stabilised by the intermolecular dipole–dipole interactions *via* carbonyl groups, which was observed in the FT-IR spectra.

Experimental

General methods

^{1}H-NMR spectra were recorded with a JEOL GX 270 spectrometer. For the FT-IR and DSC measurements, a Perkin-Elmer Paragon 1000 FT-IR spectrometer (resolution = 1 cm^{-1}) and a Seiko Instruments DSC 120 S II system (scanning rate = 2.0 °C min^{-1}) were used respectively. UV-VIS spectra were recorded with a Hewlett Packard 8453 spectrophotometer.

Synthesis of dicholesteryl esters

The dicholesteryl esters **1–*n*** ($n = 3$ and 8) were synthesised by the condensation reaction of cholesterol and commercially available corresponding diacids as described in the literature.[3] **1–*n*** ($n = 2$, 4, 5, 6, 7, and 10) were synthesised by Eglington coupling (23–63% yield)[13] of the corresponding cholesteryl esters of ω-acetylenecarboxylic acids obtained by the condensation reaction of cholesterol and the corresponding ω-acetylcarboxylic acid (32–89% yield).[14] Purification by silica-gel column chromatography (eluent: hexane–dichloromethane = 2 : 1 for **1–2**; hexane–dichloromethane = 1 : 1 for **1–4**, **1–5**, **1–6**, **1–7**; hexane–diethyl ether = 5 : 1 for **1–10**, *v*/*v*) afforded the requisite dicholesteryl compounds. The structure of each dicholesteryl ester was confirmed by the absence of an acetylenic proton signal around 1.95 ppm in the ^{1}H-NMR spectra. The purity was confirmed by thin-layer chromatography on silica gel plates (Merck 60 F254) and FAB-MS (JEOL DX-303). ^{1}H-NMR of **1–2** (270 MHz, $CDCl_3$, TMS): δ 0.68–2.03 (m, 98H), 2.21–2.32 (m, 16H), 4.60 (dd, $J = 8.9$ and 4.32 Hz, 2H, $-CH_2CH(CH_2-)O-$), 5.39 (d, $J = 4.9$ Hz, 2H, $=CH-$). In the same way, the other purified dicholesteryl esters gave satisfactory ^{1}H-NMR spectra and elemental analyses.

Preparation of coloured solid film

About 4 mg of compounds in a crystalline phase were put on a glass plate (20 × 20 × 0.18 mm) and covered with another glass plate. The compounds between the glass plates were heated to the isotropic phase and cooled to cholesteric temperatures on the hot stage (Metler FP-80 and FP-82). The film was then quickly immersed in ice–water from the hot stage to obtain solid films with a cholesteric colour. The samples for infrared spectra were prepared between a glass plate and a silicon plate. After obtaining the solid film between the two plates, the glass plate was removed for high transmittance of the infrared light.

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