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Phase transitions of cholestanyl fluoroalkanoates

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Phase transitions of cholestanyl *n*-ω-monohydrofluoroalkanoates ($C_{27}H_{47}OCO$-$(CF_2)_nCF_2H$, $n = 1, 3, 5, 7$) (CAHFA) and cholestanyl *n*-perfluoroalkanoates ($C_{27}H_{47}OCO(CF_2)_mCF_3$, $m = 0, 1, 2, 6$) (CAPFA) were studied by D.S.C. and dielectric measurements. No liquid-crystalline phase is observed for CAHFA, and in CAPFA, one monotropical liquid-crystalline phase is found on cooling only for $m = 6$.

1. Introduction

The mesomorphism of steroid-alkanoate compounds is profoundly influenced by the chemical structure of the steroid skeleton and the alkanoate. Cholesteryl *n*-alkanoates (CA) are typical liquid crystal-forming compounds [1, 2], but mesogenicity has been found to be decreased by the substitution of F atoms in the alkanoate groups [3]; the mesogenicities of the cholesteryl *n*-fluoroalkanoates were decreased relative to those of the corresponding CA. (See figure 1 which gives the chemical structures of all compounds described in this paper.) On the other hand, it is known that in the absence of the Δ^5 double bond in the cholesteryl skeleton, the mesogenicity of cholestanyl *n*-alkanoates (CAA) decreases relative to the corresponding CA [4]. In a preceding short communication [5] we reported that the above observation applies also in the relation of mesogenicities in cholestanyl *n*-ω-monohydrofluoroalkanoates (CAHFA) to those in the corresponding cholesteryl *n*-ω-monohydrofluoroalkanoates (CHFA). This paper describes further studies on phase transitions of CAHFA and cholestanyl *n*-perfluoroalkanoates (CAPFA).

2. Experimental

The $n = 1$ and 3 compounds of CAHFA and the $m = 0$, 1 and 2 compounds of CAPFA were prepared by a dehydration reaction from cholestanol and fluoroalkanoic acids. The other CAHFA ($n = 5$ and 7) and CAPFA ($m = 6$) compounds were synthesized by a dehydrogen chloride reaction from cholestanol and fluoroalkanoyl chloride in chloroform in the presence of triethylamine. The crude samples were purified by recrystallizing from ligroin and chloroform : acetone (1 : 3) solutions alternately, and the purified samples were finally recrystallized from a chloroform : acetone solution. All the samples were identified as the objectives from I.R. and N.M.R., and judged to be thoroughly purified by thin layer chromatography (developing solvent, 0·5 per cent ethyl acetate/*n*-hexane) and differential scanning calorimetry (D.S.C.).

Phase transitions were measured with a differential scanning calorimeter (Perkin Elmer, DSC-II) at a heating/cooling rate of 5 K min^{-1} in a temperature range of 120 K

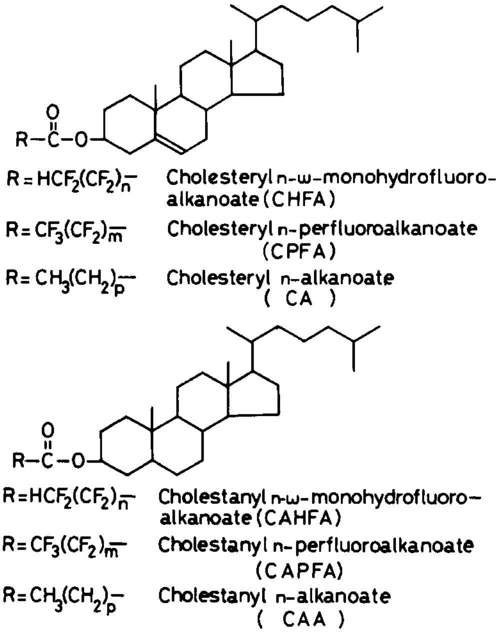

Figure 1. Chemical structures of all compounds.

through the melting point, T_m. The textures of each phase were observed with a polarizing microscope (Nikon, Optiphoto-pol XTP-11) equipped with a Mettler FP-2 hot stage at a heating/cooling rate of 1 K min^{-1}. Dielectric measurements were carried out with a Multi-Frequency LCR Meter (Hewlett Packard, Type 4274A) in the temperature range of 80 K through T_m at several frequencies between 100 Hz and 100 kHz. Electrodes were made by sucking molten compounds into two parallel gold-plated glass plates separated by a 100 μm Teflon spacer [6]. The electrode system was mounted in an electrically shielded box to avoid stray capacitance. The dielectric measurements were performed at a rate of about 0·5 K min^{-1} on both cooling and heating.

3. Results and discussion

D.S.C. curves for CAPFA homologues are shown in figure 2 and the thermodynamic parameters for their phase transitions are listed in table 1. In $m = 0$, there is an endothermic peak near 381 K on heating and an exothermic peak near 356 K on cooling, which correspond to the T_m, and the freezing point, T_f, respectively. In the crystalline phase, one small exothermic peak near 184 K is observed on the first cooling and one endothermic peak near 201 K on the second heating; this would indicate the existence of a phase transition in the crystalline state. The melting and freezing processes for $m = 1$ and 2 occur in an ordinary manner (T_m and T_f are 390 and 386 K for $m = 1$, and 388 and 385 K for $m = 2$). The melting phenomenon for $m = 6$ is complicated as follows. On the first heating from as-grown crystals, one endothermic peak occurs near 358 K, but is replaced by a peak near 359 K on the second and third heating processes. When the crystals from the melt are stored for 1 day at room temperature, peaks at 358 and 359 K appear again. (See the fourth heating process). When the storage duration is 2 weeks, the peak near 358 K is

Table 1. The thermodynamic parameters of the phase transition of CAPFA ($(C_{27}H_{47}OCO(CF_2)_mCF_3)$).

m		T_t(K)	T_m(K)	ΔS_t (J K^{-1}mol^{-1})	ΔS_m (J K^{-1}mol^{-1})		T_t(K)	T_f(K)	T_{I-L}(K)	ΔS_t (J K^{-1}mol^{-1})	ΔS_f (J K^{-1}mol^{-1})	ΔS_{I-L} (J K^{-1}mol^{-1})
0	1h		381		65	1c	184	365		2	63	
	2h	201	381	3	62	2c	187	356		3	62	
	3h	200		3								
1	1h		390		61	1c		386			42	
	2h		390		44	2c		386			42	
	3h		390		43	3c		386			42	
2	1h		388		44	1c		385			39	
	2h		388		41	2c		385			42	
6	1h		358		79	1c		329	336		51	3
	2h		359		65	2c		329	336		51	3
	3h		359		64	3c		329	336		51	3
	4h		358, 359		75	4c		329	336		51	3
	5h		358, 359		77	5c		329	336		51	3

T_t and ΔS_t, the transition temperature and the transition entropy; T_m and ΔS_m, the melting point and the melting entropy; T_f and ΔS_f, the freezing point and the freezing entropy; T_{I-L} and ΔS_{I-L}, the transition temperature from isotropic to mesomorphic state and the transition entropy from isotropic to mesomorphic state; *n*h and *n*c, *n*th heating and *n*th cooling processes.

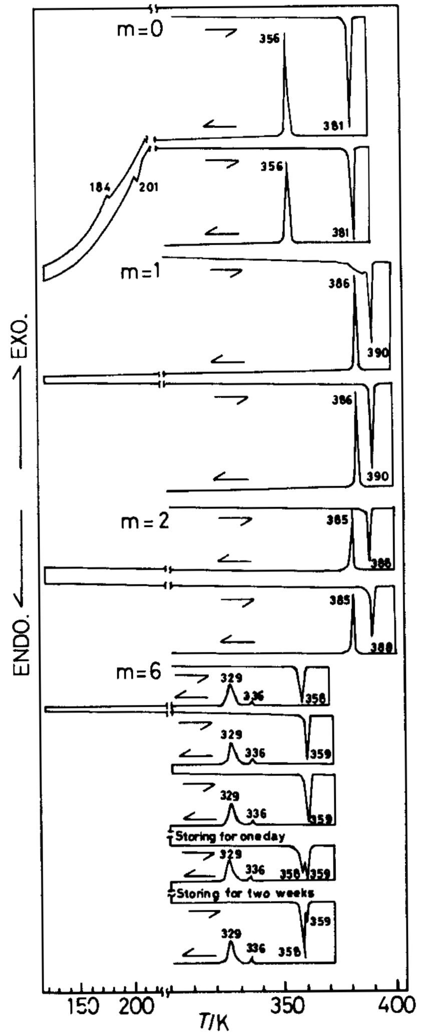

Figure 2. D.S.C. curves for CAPFA ($C_{27}H_{47}OCO(CF_2)_mCF_3$) homologues.

enhanced and the peak at 359 K is weakened. From the above results, the melting process of $m = 6$ can be interpreted thermodynamically as follows. The crystal structure of the as-grown crystals should be different from that of the crystals frozen from the melt. At room temperature, the as-grown crystals may be stable and the crystals from the melt may be metastable. Therefore, the latter crystals would change gradually to the former ones during storage at room temperature. On the other hand, near T_m, the crystals from the melt would be in a stable state because T_m for the crystals from the melt is higher than that for the as-grown crystals. In other words, the values of the free energy for the as-grown crystals may be lower than those for the crystals from the melt at room temperature, and vice versa near T_m. In the cooling process for $m = 6$, one exothermic peak is monotropically observed near 336 K with one peak at 329 K for T_f, which corresponds to the isotropic liquid–liquid-crystalline phase transition temperature, T_{I-L}. In the liquid crystalline state, a cholesteric focal conic texture with spherulitic domains was

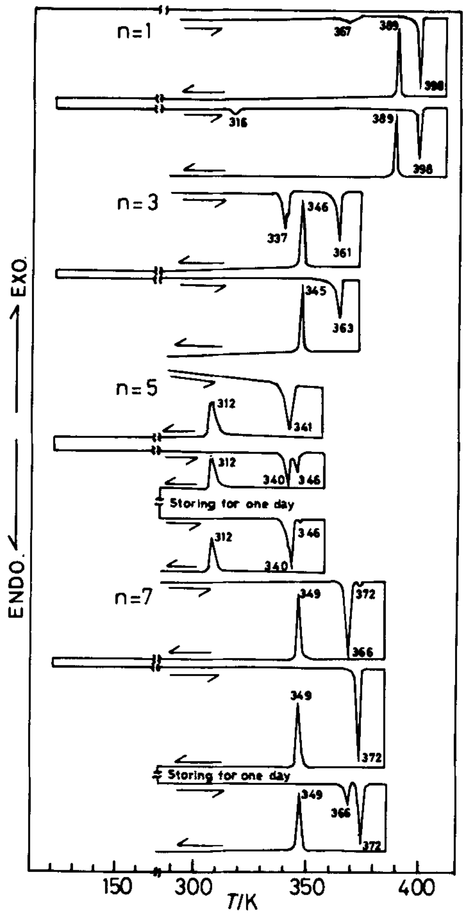

Figure 3. D.S.C. curves for CAHFA ($C_{27}H_{47}OCO(CF_2)_nCF_2H$) homologues.

observed under crossed polars, implying that the liquid-crystalline state was cholesteric.

D.S.C. curves for CAHFA are shown in figure 3 and the thermodynamic parameters for phase transitions are listed in table 2. Both an endothermic peak for T_m on heating and an exothermic peak for T_f on cooling are seen in an ordinary sense for $n = 1$ and 3 compounds. In the crystalline state, endothermic peaks are observed near 367 K for $n = 1$ and 337 K for $n = 3$ on the first heating, indicating the existence of a phase transition, but beyond the second heating these peaks disappear. These thermal hystereses suggest that the as-grown crystals transform into the crystals frozen from the melt as the phase transition temperatures on the first heating, since the entropy changes of fusion, ΔS_m, are almost the same as the entropy changes of freezing, ΔS_f, regardless of the thermal processes (see table 2).

The melting processes of $n = 5$ and 7 are similar to those for $m = 6$ of CAPFA homologues; the as-grown crystals show one endothermic peak near 341 K for $n = 5$ on the first heating, and the peak splits into two peaks near 340 and 346 K, beyond the second heating. In $n = 7$, two peaks, a peak near 366 K and a very small peak near 372 K, are observed on the first heating, but only the 372 K peak is seen on the second heating. When the samples are stored for 1 day at room temperature, the lower

Table 2. The thermodynamic parameters of the phase transition of CAHFA ($C_{27}H_{47}OCO$-$(CF_2)_nCF_2H$).

n		T_t(K)	T_m(K)	ΔS_t (J K^{-1}mol^{-1})	ΔS_m (J K^{-1}mol^{-1})		T_f(K)	ΔS (J K^{-1}mol^{-1})
1	1h	367	398	18	53	1c	389	52
	2h	316	398	8	52	2c	389	51
3	1h	337	361	40	47	1c	346	46
	2h	363			47	2c	345	47
5	1h		341		80	1c	312	77
	2h		340, 346		50, 23	2c	312	76
	3h		340, 346		76, 1·5			
7	1h		366, 372		70, 0·5	1c	349	65
	2h		372		64	2c	349	63
	3h		366, 372		12, 53			

T_t and ΔS_t, the transition temperature and the transition entropy; T_m and ΔS_m, the melting point and the melting entropy; T_f and ΔS_f, the freezing point and the freezing entropy; *n*h and *n*c, *n*th heating and *n*th cooling processes.

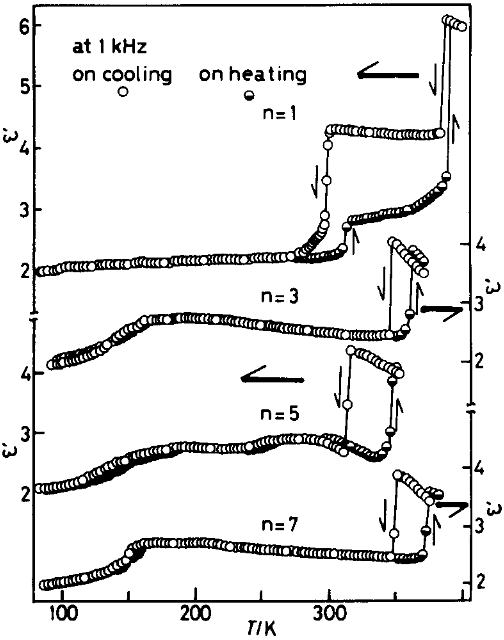

Figure 4. Temperature dependences of the dielectric constant, ε′, in the polycrystalline state of CAHFA homologues at 1 kHz.

temperature peaks are enhanced and the higher temperature peaks are weakened in both compounds. Therefore, the as-grown crystals may be stable at room temperature.

Dielectric measurements for all compounds were performed, firstly on cooling from the melt and secondly heating from 80 K. Figure 4 shows the temperature dependences of ε′ in the polycrystalline state of CAHFA compounds at 1 kHz. For

$n = 1$, the values of ε' change abruptly near 389 K on cooling and 393 K on heating, corresponding to T_f and T_m, respectively. In the crystalline state, a rapid change is observed around 310 K, which corresponds to the phase transition near 316 K on the D.S.C. curve. Although the 316 K transition is seen only on heating in the D.S.C. curve, the transition is apparently enantiotropic from the dielectric data. In the ε'-temperature plots for $n = 3$, 5 and 7, abrupt changes which correspond to the melting or freezing processes are also observed. Temperature dependences of ε' in the polycrystalline state of CAPFA homologues are shown in figure 5. In all the compounds, abrupt changes of ε' are also observed near T_m or T_f. In $m = 6$, the isotropic liquid–liquid-crystalline phase transition at 336 K is not clearly distinguished from the freezing point at 329 K by the dielectric data, since the abrupt change of ε' appears between 333 and 336 K. In the crystalline state of $m = 0$, the phase transition found in the D.S.C. curve is also observed near 190 K as an abrupt change of ε'. For $m = 2$, the values of ε' change abruptly near 300 K on cooling and near 340 K on heating, independent of frequency, suggesting the existence of a phase transition, although no phase transition is observed in the D.S.C. curve. Temperature dependences of dielectric loss, ε'', at 1 kHz are shown in figure 6 for CAHFA homologues and figure 7 for CAPFA homologues. In all the compounds, one relaxation (lower temperature relaxation) appears below 200 K and another relaxation (higher temperature relaxation) exists around 260 K in $n = 3$ and 5 of CAHFA.

Arrhenius plots for the relaxations are shown in figure 8, and the relaxation parameters are listed in table 3. The activation enthalpies, ΔH, for the lower temperature relaxations are between 16 and 36 kJ mol^{-1} for CAHFA, and about 22 kJ mol^{-1} for CAPFA. The values of ΔH for the higher temperature relaxations are 80–120 kJ mol^{-1}.

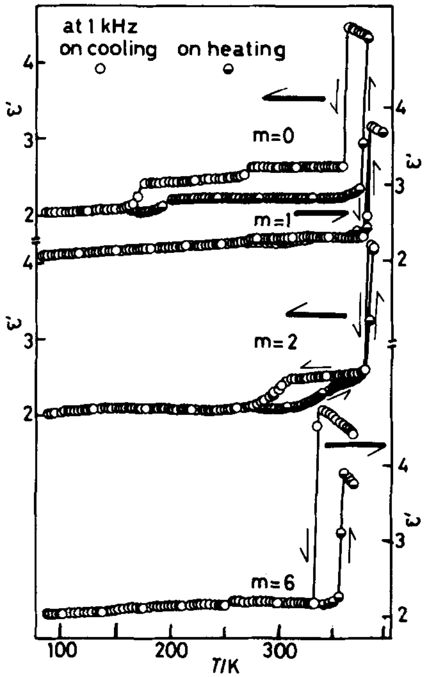

Figure 5. Temperature dependences of the dielectric constant, ε', in the polycrystalline state of CAPFA homologues at 1 kHz.

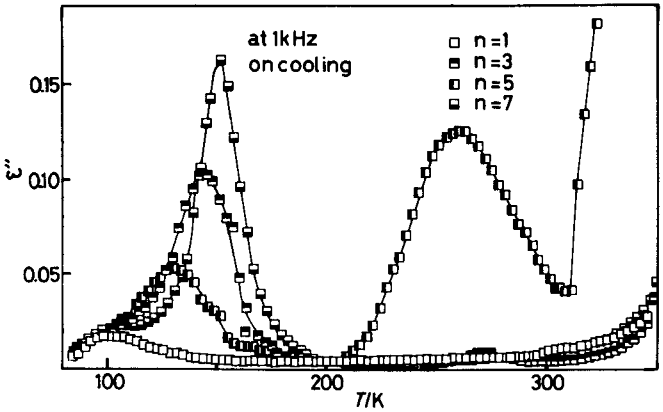

Figure 6. Temperature dependences of the dielectric loss, ε″, in the polycrystalline state of CAHFA homologues at 1 kHz.

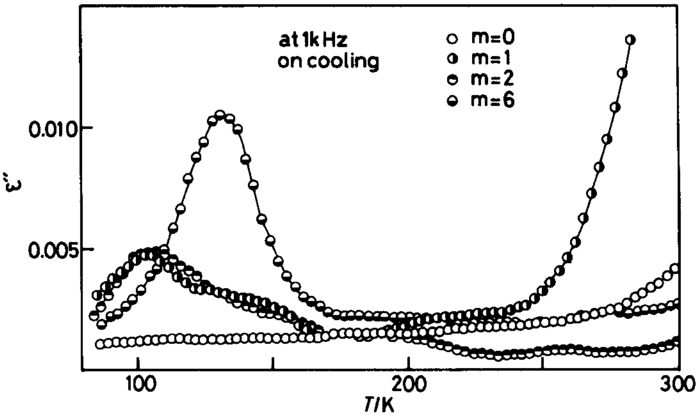

Figure 7. Temperature dependences of the dielectric loss, ε″, in the polycrystalline state of CAPFA homologues at 1 kHz.

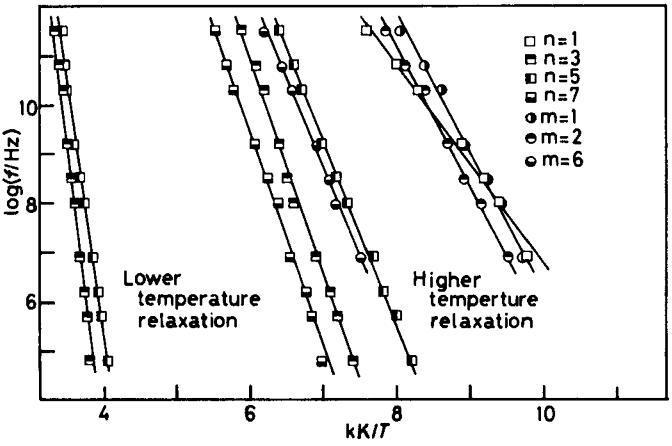

Figure 8. Arrhenius plots for all relaxations in CAHFA and CAPFA.

Table 3. Relaxation parameters for the relaxations for CAHFA ($C_{27}H_{47}OCO(CF_2)_nCF_2H$) and CAPFA ($C_{27}H_{47}OCO(CF_2)_mCF_3$) crystals.

Compound					
n	*m*	Type of relaxation†	T_{max} at 1 kHz (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
1		H	103	16	−5
3		L	144	36	84
		H	270	117	261
5		L	130	30	66
		H	260	86	160
7		L	153	36	68
	0	—	—	—	—
	1	L	103	22	52
	2	L	105	22	50
	6	L	133	28	48

†L, lower temperature relaxation; H, higher temperature relaxation.

The lower temperature relaxations are attributable to a local molecular motion of the terminal groups of fluoroalkanoate groups such as $-CF_2H$ and $-CF_3$ from the following facts: (1) The values of ΔH are in small values between 16 and 36 kJ mol^{-1}. (2) The peak heights for CAPFA are much smaller than those of CAHFA and the peak for $m = 0$ is barely observed. The perfluoroalkyl chain is non-polar but may actually have a small dipole moment by a slight deviation from the tetrahedral bond in the $-CF_3$ group [7]. This small dipole moment may be responsible for the relaxations. (3) The lower temperature relaxations have been observed in CHFA and CPFA homologues, regardless of the crystal structures [6]. The higher temperature relaxations may be related to a molecular motion of fluoroalkanoate group, since the values of ΔH are 88–120 kJ mol^{-1}, larger than those of the lower temperature relaxations.

Figures 9 and 10 show changes of phase transition temperature with the length of ester for CAHFA and CAPFA homologues, in comparison with those for CHFA and

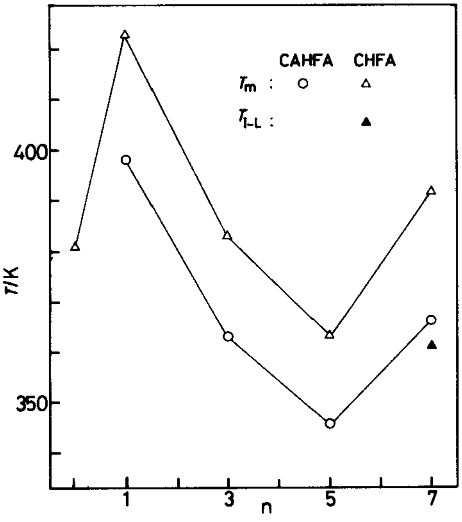

Figure 9. Plots of transition temperature versus *n* for CAHFA ($C_{27}H_{47}OCO(CF_2)_nCF_2H$) and CHFA ($C_{27}H_{45}OCO(CF_2)_nCF_2H$) homologues.

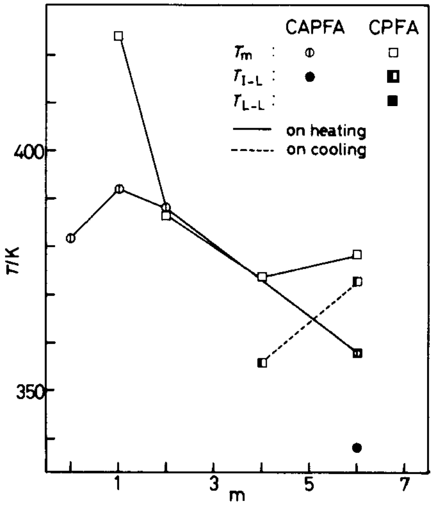

Figure 10. Plots of transition temperature versus m for CAPFA ($C_{27}H_{47}OCO(CF_2)_mCF_3$) and CPFA ($C_{27}H_{45}OCO(CF_2)_mCF_3$) homologues.

CPFA. CHFA exhibits one monotropic mesophase on cooling only for $n = 7$, but CAHFA shows no mesophase. CPFA shows one monotropic mesophase for $m = 4$ [8] and two for $m = 6$ on cooling, but CAPFA has one monotropic mesophase only for $m = 6$. Therefore, the mesogenicities of cholestanyl fluoroalkanoates are decreased relative to those of cholesteryl fluoroalkanoates, being similar to the relation in the mesogenicities between CA and CAA. This decrease in the mesogenicity of cholestanyl fluoroalkanoates may be caused by the absence of the Δ^5 double bond in the cholesteryl skeleton, which may result in a flexibility of cholesteryl skeleton. The values of T_m for CAHFA and CAPFA are lower than those of the corresponding CHFA and CPFA, except for $m = 2$. This result seems to show the increased flexibility of the cholestanyl group indirectly. On the other hand, as described already, the mesogenicities of CAHFA and CAPFA homologues are decreased by the substitution of F atoms on the alkanoates, as well as those of CHFA and CPFA homologues. Recently, we have determined the crystal structure for $m = 1$ and 4 of CPFA and $n = 1$ of CHFA by the X-ray diffraction method and have found that the fluoroalkanoate groups bend out of the director of the cholesteryl skeleton by gauche conformations of $C(\alpha)$–$C(\beta)$ and $C(\alpha)$–$(C=O)$ bonds in the crystals [9, 10]. Since the molecular conformation and packing in the crystals may prefigure those in the mesophase [11], we conclude that the decrease in the mesogenicities of cholesteryl fluoroalkanoates may be caused by the bend [9]. In the course of the X-ray diffraction work, furthermore, we found that the fluoroalkanoate chains librate thermally very much in the crystals [10, 12]. The existence of dielectric relaxations in the crystalline state seems to support the above findings. As the fluoroalkanoate chains are longer, the molecular shape of cholestanyl fluoroalkanoate may be more linear as a whole and the fluoroalkanoate may librate more strongly. In conclusion, the mesogenicities of CAHFA and CAPFA compounds may be decreased by the two hindrance factors for mesophase formation, the bend of the fluoroalkanoate out of the director of cholestanyl skeleton and the absence of the Δ^5 double bond. The appearance of mesophase in $m = 6$ of CAPFA seems to result from the fact that the fluoroalkanoate is long enough to compensate for the two hindrance factors.

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