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The Thermal Properties of 1,3,5-Trisubstituted Benzenes

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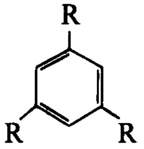
Summary-1,3,5-Tricholesteryloxycarbonyloxy(I), 1,3,5-tri-β-sitosteryloxycarbonyl(II), and 1,3,5-tricholesteryloxycarbonylbenzene(III) form mesophases, presumably the discotic cholesteric phase.

INTRODUCTION

Up to now the most mesogenic compounds have been known to have a rod-like or a lath-shape structure. However in 1977, an anisotropic fluid phase, made up of disc-like molecules, was evidenced during the thermal treatment of the molecules.[1] The discotic phase is named after the molecular shape. Generally, the discotic mesogens constitute of relatively large rigid core with high symmetric axes and plural long alkyl or alkoxy chains.[2] In 1935, Schadendorff et al. reported that 1,3,5-tricholesteryloxycarbonyloxybenzene(I) formed a cholesteric phase in the range between 143 and 161°C.[3,4] From the structural point of view, however, this compound would be expected to form not usual cholesteric phase but discotic one. In this paper we have reexamined the thermal properties of I and also the related compounds, 1,3,5-tri-β-sitosteryloxycarbonyl(II) and 1,3,5-tricholesteryloxycarbonylbenzene(III).



Compound	R
I	—OCOO(cholesteryl)
II	—COO(β-sitosteryl)
III	—COO(cholesteryl)

EXPERIMENTAL

Transition temperatures were determined using a Nikon POH polarising microscope fitted with a Mettler FP 52 heating stage and FP 5 control unit. Transition enthalpies were measured with a Daini-Seikosha SSC 560 differential scanning calorimeter. Indium (99.9%) was used as a calibration standard with a heating rate of 5 °C/min. Transition entropies were calculated by the equation; $\Delta S = \Delta H/T$.

PREPARATION

Cholesterol and β-sitosterol were purchased from Aldrich Chemical Co. and purified by silica gel column chromatography using a solvent mixture of *n*-hexane-ether (95 : 5) as an elution solvent, followed by recrystallization from absolute ethanol. I was prepared by the reaction of phloroglucinol and cholesterylchloroformate in a mixed solvent of benzene and pyridine (9 : 1). II and III were prepared by the reaction of 1,3,5-benzenetricarboxylic acid chloride and β-sitosterol or cholesterol in a mixed solvent of benzene and pyridine (1 : 1). I, II, III were purified by column chromatography on silica gel using *n*-hexane–ether (95 : 5) as an elution solvent, followed by recrystallization from a mixed solvent of *n*-hexane–ether(I) and ethanol-benzene (*ca.* 1 : 1) (II and III). The purity of the materials was checked by elementary analysis, as shown below.

	Calculated		Found	
	$C(\%)$	$H(\%)$	$C(\%)$	$H(\%)$
I	79.24	10.20	79.18	10.27
II	82.14	10.57	82.02	10.56
III	82.34	10.80	82.22	10.82

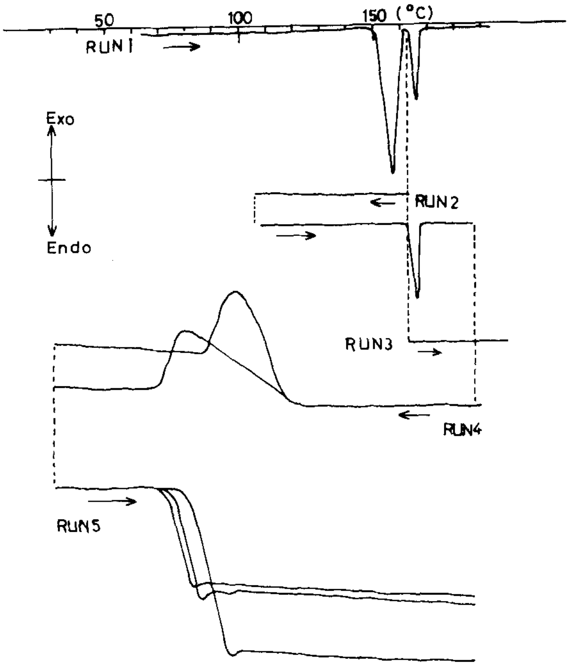


FIGURE 1 DSC thermogram for I.

RESULTS AND DISCUSSION

The DSC thermograms for I are shown in Figure 1. The thermogram on the first heating shows two endotherms at 156.9 and 165.3°C, presumably corresponding to the crystal-cholesteric (143°C) and cholesteric–isotropic (161°C) transitions.[3,4] Certainly, the liquid phase in the range between 156.9 and 165.3°C shows very weak birefringence. As shown in Figure 3a, the texture is similar to the streaked one

TABLE I

Transition temperatures, enthalpies, and entropies

	T (°C)	ΔH (KJ/mole)	ΔS (J/Kmole)	T (°C)	ΔH (KJ/mole)	ΔS (J/Kmole)
I	156.9	34.94	81.25	165.3	8.69	19.82
II	221.8	37.64	76.05	240.6	18.67	36.34
III	244.6	43.86	84.71	261.3	12.14	22.71

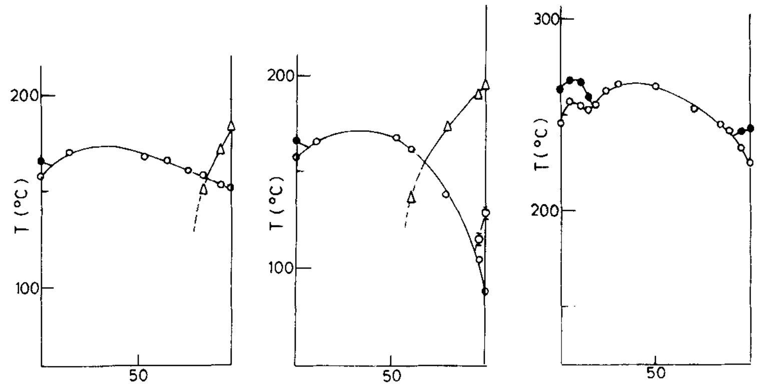


FIGURE 2 Isobaric diagrams of the mixtures for (a) I (on left) and cholesteryl benzoate (on right); (b) I (on left) and 4-pentylphenyl 4-(4-hexloxybenzoyloxy)benzoate (on right); (c) III (on left) and II (on right). ○; solid–mesophase (isotropic), △; cholesteric–isotropic, and ⊖; smectic A–cholesteric transitions.

of the usual cholesteric phase. The mesophase does not show any selective reflection in the region between 3500 and 7000 Å. The birefringence easily disappears by stirring mechanically, and does not reappear even if the sample stands for one day at 155 °C. This phenomenon is also confirmed by the DSC. As the crystal of I obtained by recrystallization from ether-*n*-hexane (1 : 1) is heated, the DSC shows two endotherms (line 1 in Figure 1). As the mesophase of I obtained by heating to 155 °C was cooled to room temperature, and then heated again to 180 °C. Thereby, the DSC thermogram showed only one endotherm at 165.3 °C (line 2), corresponding to the mesophase–isotropic transition. As the sample was stirred mechanically at ca. 155 °C, the DSC thermogram showed no peak (line 3). These phenomena are in agreement with the microscopic observations mentioned above. The lines 4 and 5 in Figure 1 demonstrate the expanded DSC curves, where the lines show disparities of the base lines in the region between 80 and 92 °C. The intensities and transition temperatures are strongly dependent on the sweep rate. Thereby, any exo- and endotherms were not observed in the region 150 and 170 °C. The transition temperature with the heating rate of 5 °C/min is 82 °C, where the Tg/Tm value is 0.83. These characteristic features on the DSC thermogram indicate that I easily forms a glassy phase of both mesophase and isotropic states. II and III also form the mesophase with similar texture to that of I. The isotropic solutions form both mesophase and crystalline states on the cooling process. As the

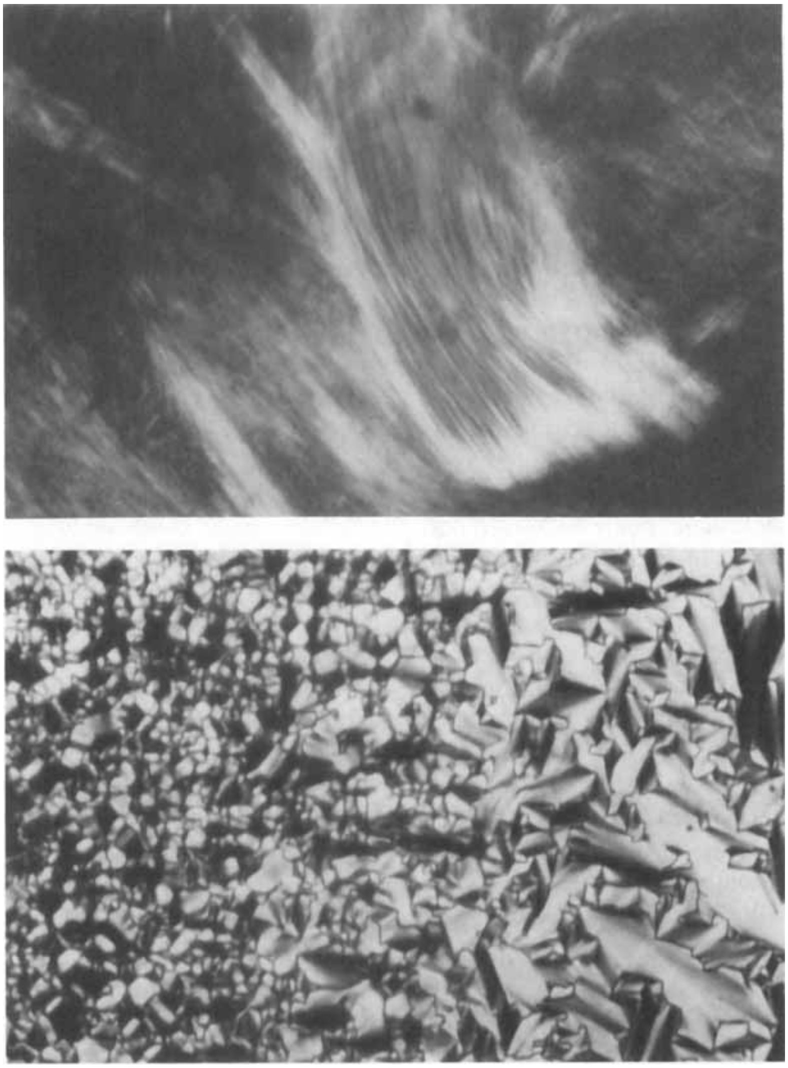


FIGURE 3 Photographs for (a) mesophase (at 160 ° C) for I; (b) cholesteric phase for the 21 mole % of I in Figure 2b (at 150 ° C).

isotropic solutions, however, are cooled by 5 °C/min, the mesophase reappears around 200 °C which is lower by 50–70 °C than the mesophase isotropic transition temperatures on heating. These facts indicate that the isotropic solutions of these compounds are also so viscous that the recovery of the anisotropic alignment of molecules is not so easy once the molecular alignment is destroyed.

The thermal data obtained by DSC thermogram on the first heating are summarized in Table I. The entropies for the mesophase–isotropic transition account for ca. 20% of the total transition entropies. The large values are frequently observed in a discotic–isotropic transition but not in a cholesteric–isotropic one.[5]

To identify the mesophase, the binary phase diagrams were examined, as shown in Figure 2. Figure 2a indicates the isobaric diagram for the mixture of I and cholesteryl benzoate. As we can see from this figure, the cholesteric phase for the benzoate is immiscible with the mesophase for I. Figure 2b indicates the isobaric diagram for the mixture of I and 4-pentylphenyl 4-(4-hexyloxybenzoyloxy)benzoate. The nematic–isotropic and smectic A–nematic phase transitions rapidly decline with increasing concentration of I. From the figure, we can assume that the mesophase for I is immiscible with the nematic and smectic A phases. The nematic phase for 4-pentylphenyl 4-(4-hexyloxybenzoyloxy)benzoate changes to the cholesteric one where the cholesteric phase shows a partially broken focal conic texture, as shown in Figure 3b. We examined the miscibility of the mesophases between II and III, as shown in Figure 2c. Unfortunately, we could not confirm their miscibility since both mesophases were hidden by the solid phase. A characteristic trend in these figures is that the solid–mesophase or isotropic transitions show convex curves.

Considering the fact that cholesteryl benzoate forms cholesteric phase[6] and 1,4-di- and 1,3-dicholesteryloxycarbonyloxybenzenes and 1,2,3-tricholesteryloxycarbonyloxybenzene do not form liquid crystal phase,[3] we can assume that the mesophase for the 1,3,5-trisubstituted benzenes is the discotic cholesteric one.[7] As well as benzene hexaalkanoates,[8] a 10% solution of I in benzene forms a lyotropic mesophase with the similar streaked texture shown in Figure 3a. Further study is underway.

References

1. S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, **9**, 471 (1977).
2. G. H. Brown, 'Advances in Liquid Crystals,' Vol. 5, p. 47, Academic Press, New York (1982).
3. E. Schadendorff and A. Verdino, *Monatch. Chem.*, **65**, 338 (1935).
4. D. Demus, H. Demus and H. Zaschke, 'Flüssige Kristalle in Tabellen,' VEB Deutscher Verlag für Grundstoff Industrie, Leipzig (1974).
5. C. Destrade, M. C. Mondon and J. Malthete, *J. Phys.* (*Paris*), **40**, C3-17 (1979).
6. Ch. Wiegand, *Z. Naturforsch.*, **4b**, 249 (1949).
7. C. Destrade, N. H. Tinh, J. Malthete and J. Jacues, *Phys. Lett.*, **79A**, 189 (1980).
8. S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, N. V. Madhusana, S. Kumar, R. Shashidhar and G. Venkatesh, *J. Phys.* (*Paris*), **40**, C3-120 (1979).