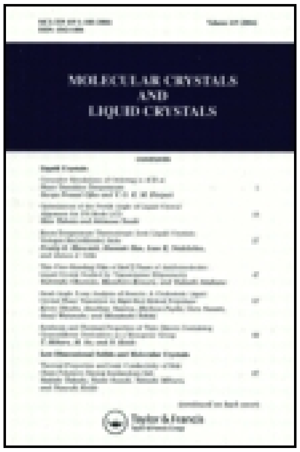

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The Thermal Properties of Some Cholesteryl and β-Sitosteryl Benzoates Incorporating Polar Terminal Groups

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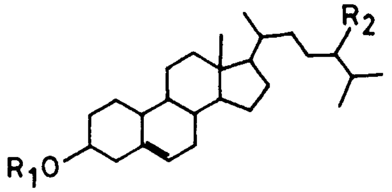
Some cholesteryl and β-sitosteryl benzoates having a nitro or a cyano group at the ortho, meta, and para positions, and their related compounds have been prepared. When a cyano or a nitro group is introduced at the para position, the molecules tend to display a smectic A phase and a highly stable cholesteric one. The smectic A phase has a bilayer arrangement of the molecules, and is isomorphous with the S_{A2} phase of polar liquid crystals such as DB6, and has no affinity with the S_{A1} phase of non-polar liquid crystals such as usual steroid esters and benzenoid compounds, or the S_{Ad} phase of CBOOA, 8OCB, and reentrant mesogens. The S_{A2} phase is also formed by the ortho- and meta-nitro substituted derivatives. The polar interaction around the benzoate moiety is proposed to be responsible for the formation of the antiparallel dimers.

Keywords: mesomorphic properties, smectic A phase, steroid esters

It has been known that liquid crystals having a very polar group such as cyano or a nitro group at the terminal position form antiparallel dimers, and display quite interesting variations of the molecular arrangement in the smectic A phases, i.e., the monolayer (S_{A1}), bilayer (S_{A2}), partially bilayer (S_{Ad}), and antiphase ($S_{\tilde{A}}$).[1,2] The intermolecular electrostatic interaction around the functional groups, i.e., the polar terminal group and linkages such as an ester or an azomethine group, has been proposed to be responsible for the mesomorphisms.

It is well known that most steroid ester compounds form only a monolayer-type arrangement of the molecules in the smectic A phase, since the steroid cores are considerably bulky and less polar compared with usual benzenoid compounds. Up to now, some steroid esters incorporating a nitro or a cyano group have been prepared,[3] but the characterization of the mesophases has not been done.

In this work, the thermal properties of some steroid esters which are summarized in Table I, have been described, and the role of the cyano or the nitro group has been discussed. The structures of cholesterol and β-sitosterol are shown below.



Cholesterol $R_1 = H$ $R_2 = H$
β-Sitosterol $R_1 = H$ $R_2 = C_2H_5$

EXPERIMENTALS

Materials

The preparation of materials was described in an earlier paper.[4] The elementary analysis data are summarized in Table I.

TABLE I

Elementary analysis data

		Calculated (%)			Found (%)		
Compound	Formula	C	H	N	C	H	N
1	$C_{35}H_{49}NO_2$	81.50	9.58	2.71	81.41	9.51	2.58
2	$C_{35}H_{49}NO_2$	81.50	9.58	2.71	81.43	9.49	2.52
3	$C_{34}H_{49}NO_4$	76.22	9.22	2.61	76.22	9.02	2.43
4	$C_{34}N_{49}NO_4$	76.22	9.22	2.61	76.13	9.06	2.41
5	$C_{34}H_{49}NO_4$	76.22	9.22	2.61	76.09	9.16	2.49
6	$C_{41}H_{53}NO_5$	76.96	8.35	2.19	76.90	8.24	2.09
7	$C_{36}H_{53}NO_4$	76.69	9.48	2.48	76.55	9.42	2.38
8	$C_{43}H_{58}O_3$	82.91	9.39		82.93	9.32	
9	$C_{42}H_{58}O_2$	84.79	9.83		84.70	9.72	

Method

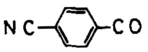
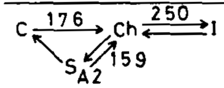
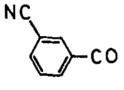
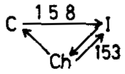
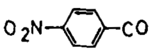
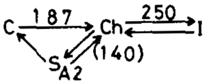
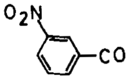
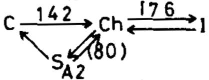
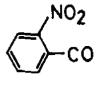
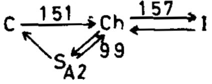
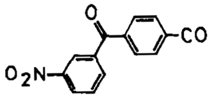
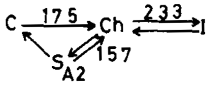
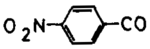
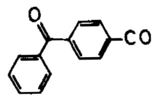
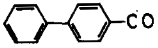
Transition temperatures were determined by using a Nikon Model POH polarising microscope fitted with a Mettler FP 52 heating stage and an FP 5 control unit, and a Daini-seikosha SSC-560 differential scanning calorimeter (DSC).

RESULTS

The transition temperatures for the present compounds are summarized in Table II.

TABLE II

C, S_A, *Ch*, and I represent crystal, smectic A and cholesteric phases, and isotropic solution, respectively. Parentheses indicate the extrapolated transition temperatures.

Compounds	R_1	R_2	Transition Temperatures (°C)
1[*1]		H	
2		H	
3[*1]		H	
4[*2]		H	
5		H	
6		H	
7[*3]		C_2H_5	$C \xrightleftharpoons{182} S_{A2} \xrightleftharpoons{187} Ch \xrightleftharpoons{250} I$
8		C_2H_5	$C \xrightleftharpoons{127} S_A \xrightleftharpoons{133} Ch \xrightleftharpoons{170} I$
9[*3]		C_2H_5	$C \xrightleftharpoons{163} S_A \xrightleftharpoons{192} Ch \xrightleftharpoons{269} I$

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[1] Ref. 5.
[2] Ref. 6.
[3] Ref. 7.

The cyano compound **1** shows a monotropic S_A phase with a somewhat broken-fan texture and a highly stable Ch one. The S_A-Ch transition could not be detected by the DSC thermogram because of the low latent heat for the transition. The 3-cyanobenzoate ester **2** shows only a monotropic Ch phase. The fluid obtained by melting recrystallized at ca. 150°C, and showed no smectic phase on the cooling stage.

The 4-nitrobenzoate ester **3** also exhibits a monotropic S_A phase, and the formation was competitive with recrystallization on the cooling stage. In order to make sure, the S_A-Ch transition temperature was evaluated from an extrapolation in the binary phase diagram of **1** and **3**. For the 3-nitrobenzoate ester **4**, the formation of the S_A phase was also competitive with recrystallization, so that the value in the table was evaluated from the binary phase diagram, as shown in Figure 2. The 2-nitrobenzoate ester **5** also exhibits a monotropic S_A phase, which can be detected by microscopic observation. Cholesteryl 4-(3-nitrobenzoyl)benzoate ester **6** shows a Ch phase and a monotropic S_A one. The monotropic S_A phase was stable for several hours at room temperature, so that **6** was frequently used for the miscibility experiment of smectic A phases, as shown in Figures 1 and 2. The 4-nitrobenzoate ester of β-sitosterol **7** shows enantiotropic S_A and Ch phases, where the S_A-Ch transition can be detected by microscopic observation.

The non-polar β-sitosteryl esters, **8** and **9** also show both S_A and Ch phases enantiotropically, where the S_A-Ch transitions are detectable by both DSC and microscopic observation.

In order to characterize these smectic phases, we examined some binary phase diagrams, as shown in Figures 1 and 2.

In Figure 1, miscibility relations between the mesophases of steroid esters and benzenoid compounds are illustrated. In Figure 1a, both S_A phases of non-polar liquid crystals are isomorphous with a broad maximum around the center of the diagram, indicating that both S_A phases have a monolayer-type arrangement of the molecules. However, the S_A-phase of polar liquid crystal **6** is immiscible with the S_{A1} phase of 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate[8] and the S_{Ad} phase of *N*-[4-(4-octyloxybenzoyloxy)benzylidene]-4-cyanoaniline (Figures 1b and 1d).[9] In both figures, the S_A phases are separated by a large discontinuous region. The binary mixtures involving CBOOA or 8OCB showed similar phase behavior. On the other hand, the S_A phase of **6** is isomorphous with the S_{A2} phase of 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (DB6),[10] though the S_A-

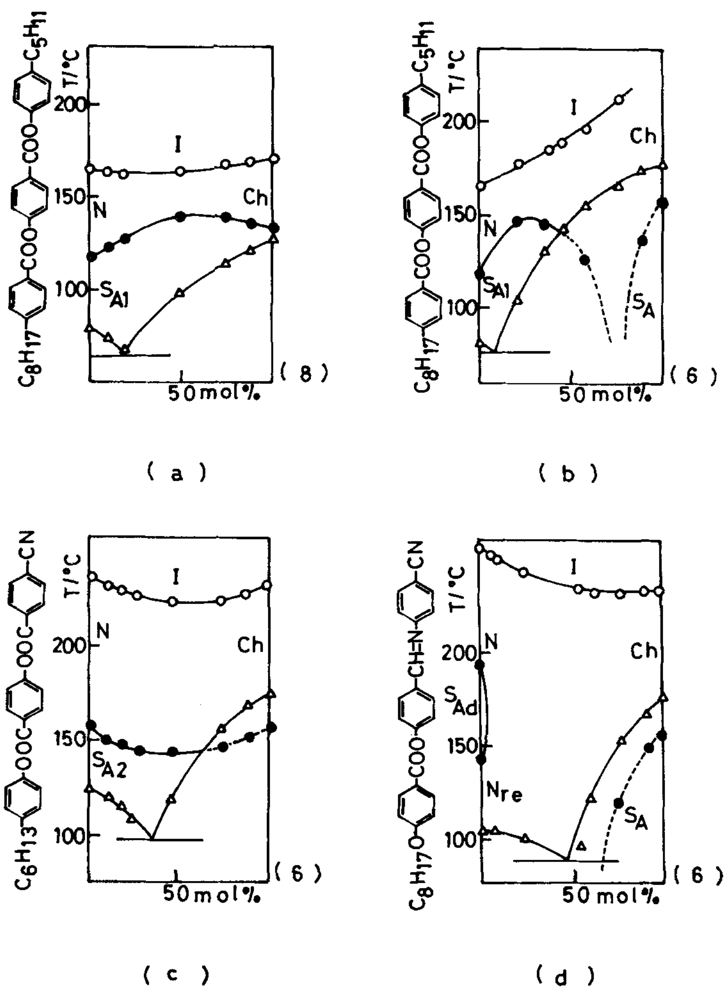

FIGURE 1 The miscibility diagrams for the mixtures of: a) 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate (on left) and **8** (on right), b) 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate (on left) and **6** (on right), c) 4-hexylphenyl 4-(4-cyanobenzoyloxy)benzoate (on left) and **6** (on right), d) *N*-[4-(4-octyloxybenzoyloxy)-benzylidene]-4-cyanoaniline (on left) and **6** (on right). Dashed lines indicate monotropic transitions.

Ch transition temperatures show a downward convexity around the center of the diagram (Figure 1c).

A quite similar phase behavior could be observed in the binary phase diagrams of steroid esters, and the results are shown in Figure 2.

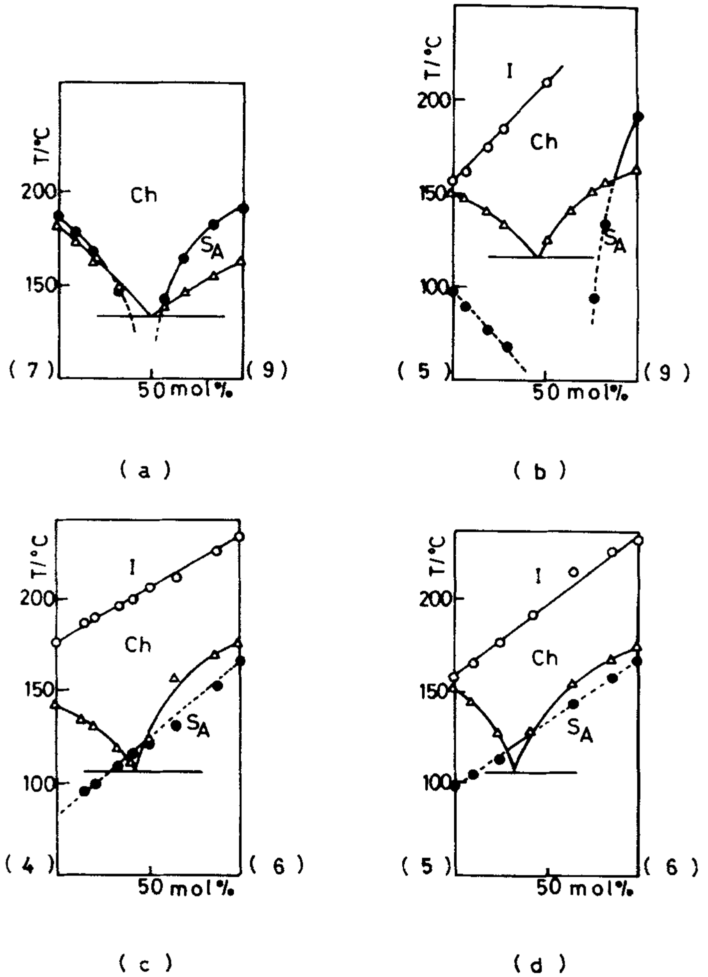

FIGURE 2 The miscibility diagrams for the mixtures of: a) **7** (on left) and **9** (on right), b) **5** (on left) and **9** (on right), c) **4** (on left) and **6** (on right), d) **5** (on left) and **6** (on right). Dashed lines indicate monotropic transitions.

The S_A phase of the polar esters, **1**–**7**, has no affinity with the S_{A1} phase of the non-polar esters, **8**–**9**. Examples are shown in Figures 2a and 2b, where the S_A-Ch transition temperatures are discontinuous, giving rise to a wide cholesteric region. On the other hand, the S_A phase of the polar esters, **1**–**7**, is completely isomorphous in each case, where the S_A-Ch transition temperatures show a linear correlation with additivity, as shown in Figures 2c and 2d. The S_A-Ch transition temperatures for the binary mixtures of **1**–**6**, **3**–**6**, and **1**–**3** show quite similar trends, while some portions of the transitions are hidden by the crystalline phase.

DISCUSSION

It is known that compounds incorporating a cyano or a nitro group have strong dipole moments directing the long axis of the molecules.[11]

CH_3CN	3.92	CH_3NO_2	3.46
C_6H_5CN	4.40	$C_6H_5NO_2$	4.22

(Debye unit: 1D $= 3.3 \times 10^{-30}$ Cm)

The dipole moments are strong enough to form the associated dimers of the molecules. In liquid crystalline materials, the molecules having a cyano or a nitro group at the terminal position tend to form antiparallel dimers not only in various kinds of liquid crystalline phases but also in isotropic liquid. Such molecular association is realized by an enhancement of the thermal stabilities of liquid crystalline phases, or very interesting mesomorphisms near nematic, smectic A, and smectic C phases.[1,2] On the other hand, the cyano and nitro groups attached to the lateral position of liquid crystals scarcely show such apparent effects on the mesomorphic properties. The effects of these substituents on the mesomorphic properties are usually discussed only in terms of an increased molecular breadth.[12]

In general, the steroid esters having no polar group show a smectic A phase with a monolayer arrangement of the molecule (S_{A1}).[13] The β-sitosteryl esters, **8** and **9** are such cases. Of course, the S_{A1} phase has similar thermal properties to non-polar benzenoid liquid crystals. An example is shown in Figure 1a, where both S_A phases of **8** and 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate are completely isomorphous, and the S_A-Ch(N) transition temperatures give an almost straight line. When a cyano or a nitro group is introduced at the para position of the aromatic portions, i.e., compounds, **1**, **3**, and **7**, the molecules tend to form a more stable smectic A phase than the non-polar steroid esters. The S_A phase of the steroid esters **1**, **3**, and **7** is isomorphous with the S_{A2} phase of the benzenoid compounds (Figure 1c), while the phase is immiscible with the S_{A1} phase of steroid compounds, **8** and **9** (Figure 2a), and also non-polar benzenoid compounds, i.e., 4-pentylphenyl 4-(4-octylbenzoyloxy)benzoate (Figure 1b). Furthermore, the S_{A2} phase of the polar steroid esters is immiscible with the S_{Ad} phase of polar benzenoid liquid crystals such as *N*-[4-(4-octyloxybenzoyloxy)benzylidene]-4-cyanoaniline (Figure 1d). Thermodynamic behavior has been commonly observed in benzenoid liquid crystals,[1,2] and the S_A phase of the polar steroid esters is, therefore, assigned to a S_{A2} one. The assignment precisely agrees with the X-ray results of **1**.[14] The present compounds **1**, **3** and **7**, are the first instances of the steroid ester compounds exhibiting the S_{A2} phase.

For compound **6**, the nitro group is situated at the 3′ position of 4-benzoylbenzoic acid, and two rotational isomers are considered with respect to the nitro group, as shown in Figure 3.

Two rotamers must be almost equivalent from the energetical point of view, and the equilibrium constant must be close to unity. In rotamer [A], the nitro group situates parallel to the long molecular axis, and increases anisotropic polarity and polarisability parallel to the long molecular axis. On the other hand, the rotamer [B] should be very unfavorable for mesomorphic phenomena, since the nitro group remarkably increases the molecular breadth. Considering the fact that **6** exhibits highly stable Ch and S_{A2} phases, the rotamer [A] must be preferable to [B] in the mesophases.[15]

Some interesting facts are recognized in the thermal properties of the ortho- and meta-nitro derivatives **4** and **5**. For both compounds, the Ch-I transition temperatures are quite low compared with those of the para substituted compounds **1**, **3**, and **7**, probably due to the expanded molecular breadth. However, these also exhibit the monotropic S_A phase. The S_A phase is isomorphous with the S_{A2} phase of compounds **1**, **3**, and **7**, as shown in Figures 2c and 2d, where the S_{A2}-Ch transition temperatures show a linear correlation with additivity, indicating very clearly that the ortho- and meta-nitro substituted compounds also form the associated dimers, and the S_A phase has the bilayer arrangement of the molecules. The models for the associated dimers are shown in Figure 4.

In the ortho and meta derivatives, the dipole–dipole interaction is

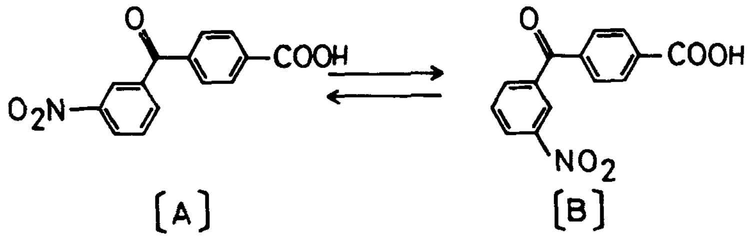

FIGURE 3 Rotational isomerism for 4-(3-nitrobenzoyl)benzoic acid.

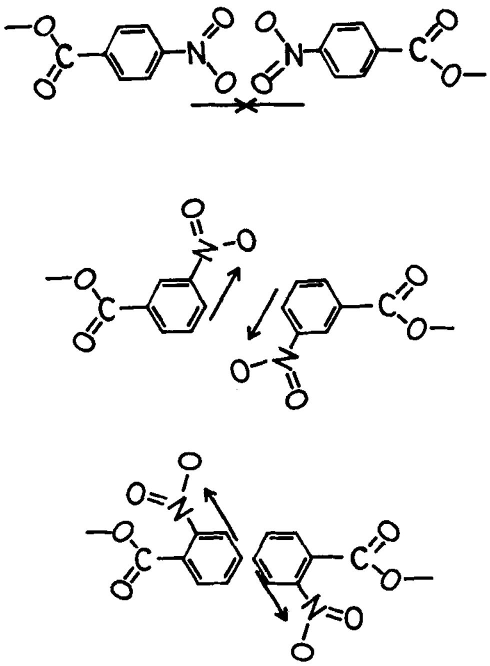

FIGURE 4 Formation of antiparallel dimers for 3–5. Arrows indicate dipole moments arising from the nitro group.

assumed to be responsible for the formation of the dimers, while the dipole moments arising from the nitro groups occur at an angle with respect to the long molecular axis.

In this paper, we have examined the miscibility of the mesophases between steroidal and benzenoid liquid crystals. The following facts are noteworthy. For the Ch(N) phase, a difference in the molecular geometry appears to be less important for the miscibility, while the Ch(N)-I transition temperatures sometimes show a weak downward convexity around the center of the diagrams (for example, Figures 1a and 1c). For the smectic A phase, the geometrical difference is also a minor factor for the miscibility. For example, the S_{A1}-Ch(N) and S_{A2}-Ch(N) transition temperatures show only weak deviation from linearity in Figures 1a and 1c. For the smectic A phase, however, the difference in polarity of the molecules, i.e., the molecular arrangement, is quite important in determining the miscibility relation. In Figure 1b, for example, the S_{A1} and S_{A2} phases are discontinuous, and have no S_{A1}-S_{A2} transition nor **vice-versa**. Similarly, the S_{A1} and S_{A2} phases are also discontinuous in Figures 2a and 2b, in spite of their structural similarities. On the other hand, both S_{A2} phases of steroidal esters and benzenoid compounds have good miscibility with each other (Figures 1c, 2c, and 2d), but the S_{A2} phase is discontinuous with the S_{Ad} phase (Figure 1d). These trends are frequently observed in benzenoid liquid crystals. It is concluded that in binary mixtures, the thermal properties of the smectic A phase are strongly dependent on the polarity of the molecules, and almost independent of the molecular geometry.

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13. The molecules in the S_A phase of cholesteryl alkanoates are arranged with adjacent molecules antiparallel, and the layer spacings are less than the fully extended molecular lengths. In this paper, therefore, the molecular arrangements are called "S_{A1}" phase, similar to those of non-polar benzenoid liquid crystals. In fact, the thermal properties of both S_{A1} phases are similar to each other (see Figure 1a). J. H. Wendorff and F. P. Price, *Mol. Cryst. Liq. Cryst.*, **24**, 129 (1973). J. A. W. Barnard and J. E. Lydon, *ibid.*, **26**, 285 (1974). B. M. Craven and G. T. DeTitta, *J. C. S. Perkin II*, 814 (1976).
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