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Mesomorphic properties of troponoid esters and amides with cholest-5-ene-3*β*-carboxylic acid moiety

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Troponoid esters and amides connected with cholest-5-ene-3*β*-carboxylic acid have been synthesized to characterize their mesomorphic properties and to compare them with those of the corresponding benzenoids. 5-Alkoxytroponyl esters and amides with a long alkoxy group exhibited a twist grain boundary A* phase, as well as chiral nematic and smectic A* (SmA*) phases. The corresponding benzenoid esters exhibit SmA* and blue phases and the benzenoid amides only a SmA* phase. The differences between the mesomorphic properties are discussed in terms of the structural features of the core.

1. Introduction

It is known that compounds with a nematic (N) phase exhibit a chiral nematic (N*) phase with a helical structure when a chiral component is added or a chiral segment is incorporated into the molecular structure [1], whereas N phases change to lamellar phases when the strength of the lateral interaction is increased. When these properties of formation of both a helical and lamellar structure are incorporated into the same molecule, they compete to overcome each other since they cannot coexist. When a helical structure predominates a lamellar one, an N* phase should appear, whereas a smectic (Sm) phase should be observed when the lamellar structure overcomes the helical one [2–5].

In this paper, we selected seven-membered (troponoid) structures as a part of the core structure of liquid crystals because troponoids usually tend to form layer structures [6]. This might be due to the fact that troponoids have a large dipole moment (e.g. 3.5 D for tropolone) [7]. The incompatibility between the helical and the lamellar structures should be increased to prepare the formation of frustrated phases, such as twist grain boundary (TGB) phases and blue phases (BP) when these polar troponoids are used as a part of the core structure. Previously, we have observed that monocyclic troponoids with an acyloxy group at the C-2 position show monotropic smectic A (SmA) phases where an acyl group migration, so-called [1, 9]-sigmatropy, played a role in assisting the appearance of mesophases [8]. In this aspect, cholest-5-ene-3*β*-carboylic acid was chosen as a chiral group because it forms a [1, 9]-sigmatropic system. The mesomorphic properties of the benzenoid ester (**1**, see scheme 1) with cholest-5-ene-3*β*-carboxylic acid were reported by Harwood *et al.* [9]. All benzenoid compounds show a BP or a twist grain boundary A* (TGBA*) phase, as summarized in table 1.

2. Results and discussion

2.1. *Synthesis*

5-Substituted troponyl cholest-5-ene-3*β*-carboxylates (**2**–**4**) and the corresponding troponoid (**5**) and benzenoid amides (**6**) were synthesized by reaction of cholest-5-ene-3*β*-carboxylic acid and the appropriate 5-substituted tropolones and 2-aminotropones and 4-alkoxyanilines using DCC (*N,N′*-dicyclohexylcarbodiimide) or EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide) and DMAP (4-*N,N*-dimethylaminopyridine).

2.2. *Mesomorphic properties of esters*

The phase transition temperatures were determined by differential scanning calorimetry (DSC). The typical DSC thermographs of compounds **2e** and **3** are shown in figure 1. The clearing peak of compound **2e** is rather small, suggesting an N–isotropic (Iso) liquid transition, whereas that of **3** is larger, suggesting a Sm–Iso transition. The mesophases were assigned by textural

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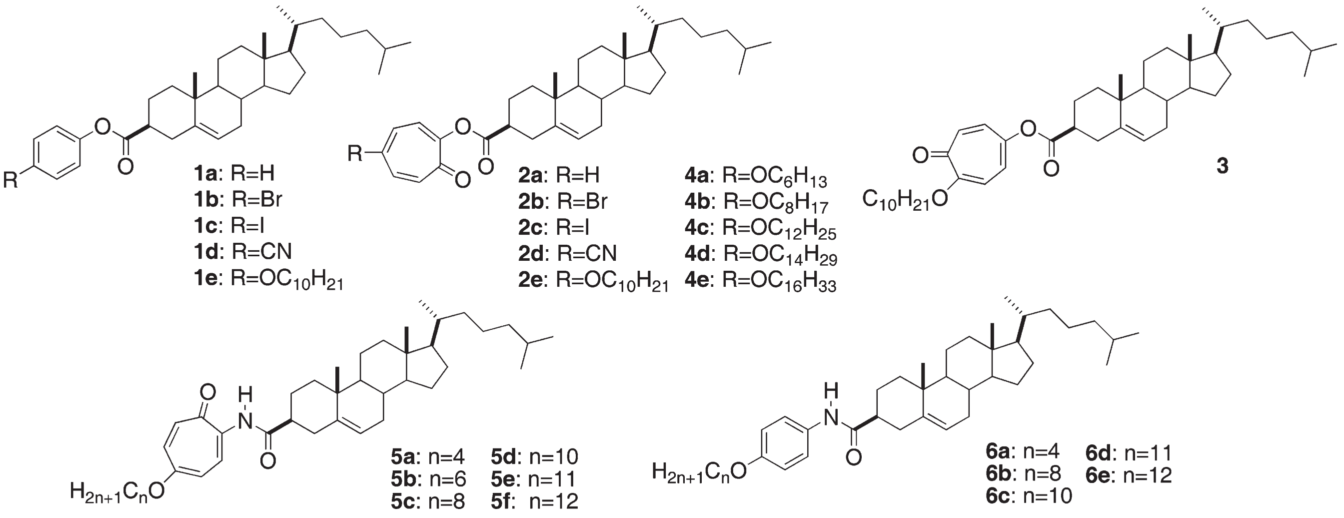


Scheme 1. Structures of cholesten-3β-carboxylates.

Table 1. Transition temperatures (°C) of benzenoid (**1**)[a] and troponoid esters (**2, 3**)[b].

1a	Cr • 106.7 • N* • 175.2 • BP • 176.3 • Iso	**2a**	Cr$_1$ • 141.6 • Cr$_2$ • 185.9 • (SmA* • 178.5 •) N* • 201.2 • Iso
1b	Cr • 109.2 • N* • 244.4 • BP • 245.1 • Iso	**2b**	Cr • 198.4 • N* • >223 • Dec
1c	Cr • 127.8 • N* • 244.4 • BP • 253.6 • Iso	**2c**	Cr • 215.9 • N* • >220.5 • Dec
1d	Cr • 162.5 • SmA* • 189.0 • TGBA* • 189.2 • N* • 284.1 • Iso	**2d**	Cr • 199.3 • SmA* • >232 • Dec
1e	Cr • 64.2 • SmA* • 218.7 • (BP • 217.6 •) Iso	**2e**	Cr • 113.9 • SmA* • 162.1[c] • TGBA* • 163.9[c] • N* • 206.6 • Iso
		3	Cr • 125.2 • SmA* • 205.6 • Iso

[a] Reference 9. [b] Determined by DSC. [c] Determined by microscopic observation on heating process.

observation using a polarizing optical microscope and X-ray diffraction (XRD) studies. The transition temperatures and phase behaviours of the troponoid esters (**2** and **3**) are given in table 1.

Compounds **2a**–**2c** showed an N* phase and compound **2a** also exhibited a monotropic SmA* phase. Compound **2d** exhibited only a SmA* phase, whereas compound **2e** had N*, SmA* and TGBA* phases. Compound **3**, an isomer of **2e**, showed a SmA* phase. The typical optical textures of compound **2e** are shown in figure 2. Homeotropic textures are shown in figure 2a, which was assigned to SmA* phases since a uniaxial conoscopic figure was observed and the homeotropic textures are changed to fan textures by shearing. In figure 2b, long strands of a TGBA* phase start to grow into the homeotropic phases [2] and the long strands of the TGBA* phase begin to change to the N* phases in figure 2c.

An XRD pattern of compound **2e** taken at 156°C on second heating is shown in figure 3. Two reflections appear around $2\theta=2.5^\circ$ (100) and $2\theta=5.0^\circ$ (200), together with a diffuse halo, which corresponds to the distance between neighbouring molecules. The layer spacing of **2e** is 35.1 Å, whereas the calculated molecular length from MM2 calculations is 38.7 Å. Thus, the layer spacing is slightly smaller than the extended molecular length, suggesting a partially interdigitated packing model. We propose that a head-to-tail structure cancels the repulsive interaction of the polar troponoid structures, where the cholesteryl moiety and the alkyl side chain of the tropone ring overlap.

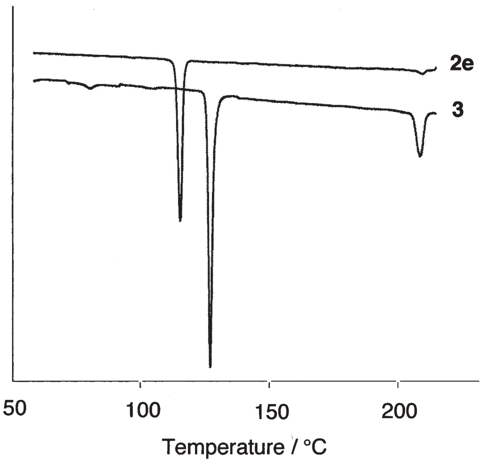


Figure 1. DSC curves of compound **2e** and **3**.

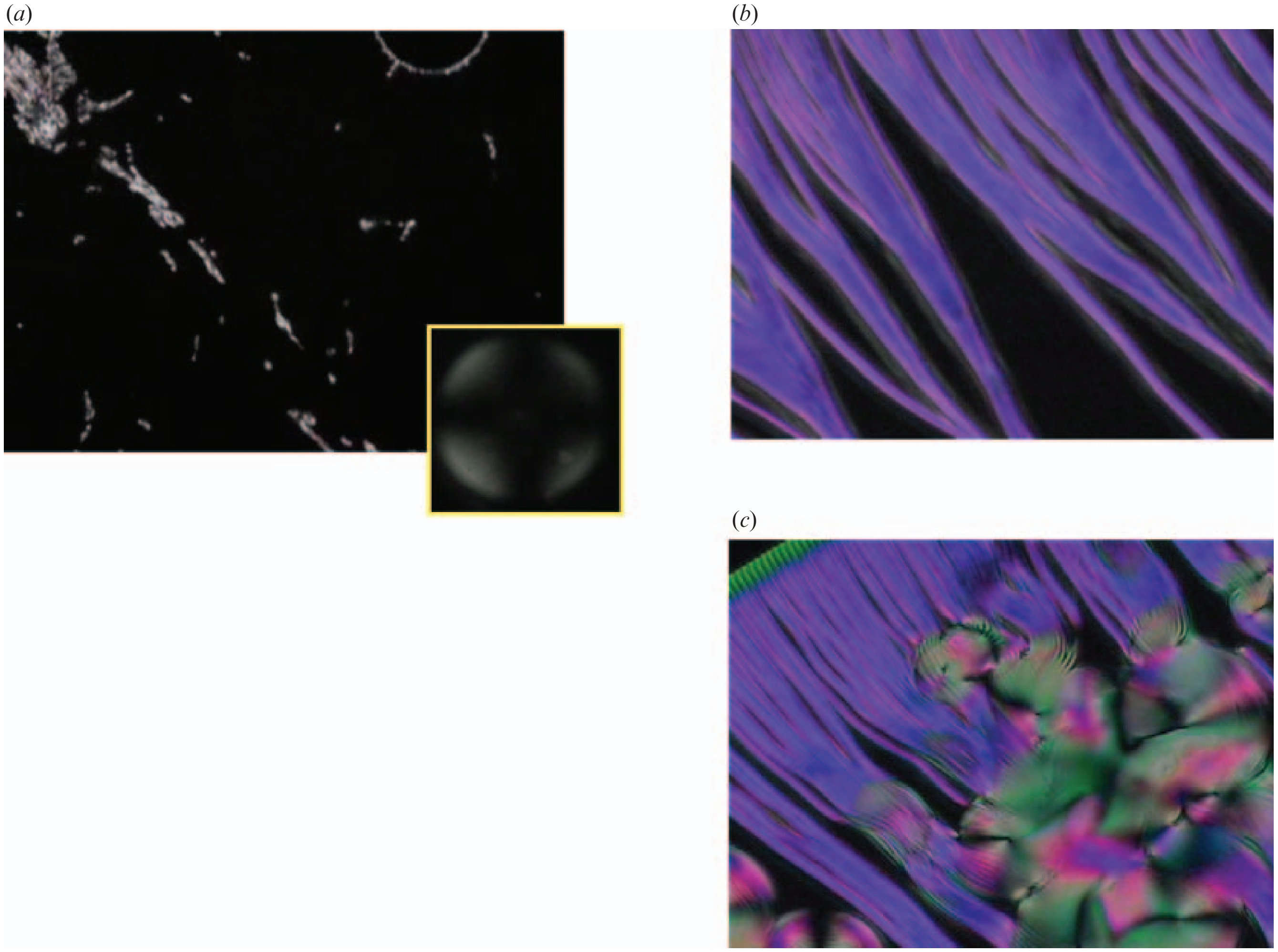


Figure 2. Photomicrographs of compound **2e** on second heating: (a) at 156°C; (b) at 163.2°C; (c) at 163.9°C.

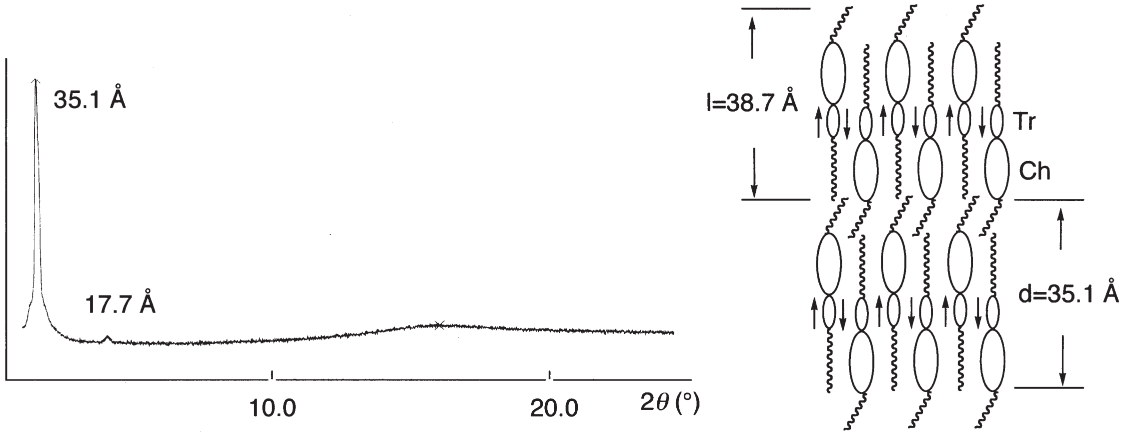


Figure 3. XRD of the SmA* phase at 156°C on second heating of compound **2e** and packing model. Tr=tropone ring; Ch=cholesteryl moiety. Arrows indicate the direction of the dipole.

As shown in table 1, only compound **2e** with an alkoxyl group showed a TGBA* phase. Therefore, we changed the length of the alkoxyl chain to study the effect of chain length on appearance of the mesophases. The result is shown in table 2, where compound **4c** with a tetradecyloxy group has a TGBA* phase. When compounds **4** have a shorter alkoxyl group, they show an N* phase, whereas compounds **4** with a longer alkoxyl group have lamellar phases.

Table 2. Transition temperatures (°C) of troponoid esters (**4**) and **2e**[a].

4a n=6	Cr • 133.2 • N* • 226.0 • Iso
4b n=8	Cr • 124.3 • N* • 216.9 • Iso
2e n=10	Cr • 113.9 • SmA* • 162.1[b] • TGBA* • 163.9[b] • N* • 206.6 • Iso
4c n=12	Cr$_1$ • 42.2 • Cr$_1$ • 112.3 • SmA* • 191.2[b] • TGBA* • 191.6[b] • N* • 203.0 • Iso
4d n=14	Cr • 119.2 • SmA* • 193.3 • N* • 200.9 • Iso
4e n=16	Cr • 116.0 • SmC* • 150.0 • SmA* • 193.6 • Iso

[a] Determined by DSC. [b] Determined by microscopic observation on heating process.

2.3. *Mesomorphic properties of amides*

Since we observed that 5-alkoxytroponoids had a TGBA* phase, troponoid amides **5** with an alkoxy group at the C-5 position were synthesized together with the corresponding benzenoid amides **6**. The results are summarized in table 3, where the troponoid amides **5** with a long alkoxy group showed a TGBA* phase as well as SmA* and N* phases. The texture of the TGBA* phase of compound **5f** is shown in figure 4. The XRD data of compound **5f** showed that the SmA* phase had a layer spacing of 36.4 Å at 150°C. Since the calculated molecular length is 39.7 Å, a head-to-tail structure is proposed in figure 4b, where the dipole–dipole repulsion between the troponoid parts is cancelled.

On the other hand, benzenoid amides (**6**) exhibit only a SmA* phase. Their texture is shown in figure 5. The XRD data of **6e** indicated that it had a partially interdigitated structure since the layer spacing is 31.4 Å and the calculated molecular length is 34.1 Å. Since the dipole moment of the benzene ring of benzenoid amide **6** is not so large, the orientation of molecules **6** should be random, as shown in figure 5b. In this packing

Table 3. Transition temperatures (°C) of troponoid (**5**) and benzenoid amides (**6**)[a].

5a n=4	Cr • 145 • N* • 240 • Iso	**6a** n=4	Cr • 147 • SmA* • 278 • Iso
5b n=6	Cr • 137 • N* • 240 • Iso	**6b** n=8	Cr • 192 • SmA* • 275 • Iso
5c n=8	Cr • 114 • N* • 221 • Iso	**6c** n=10	Cr • 159 • SmA* • 264 • Iso
5d n=10	Cr • 100 • SmA* • 216 • Iso	**6d** n=11	Cr • 157 • SmA* • 256 • Iso
5e n=11	Cr • 121.5 • SmA* • 157[b] • TGBA* • 158.5[b] • N* • 293.1 • Iso	**6e** n=12	Cr • 158 • SmA* • 255 • Iso
5f n=12	Cr • 140 • SmA* • 170[b] • TGBA* • 171[b] • N* • 200 • Iso		

[a] Determined by DSC. [b] Determined by microscopic observation on heating process.

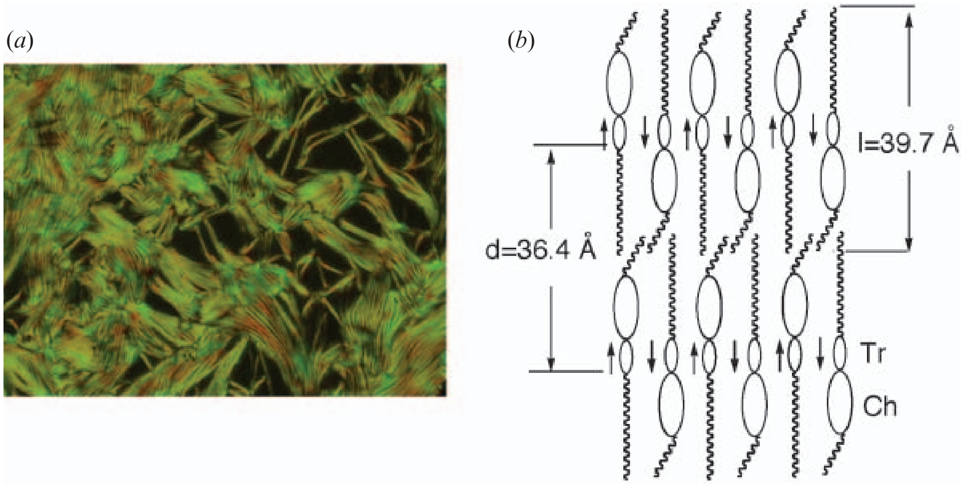


Figure 4. (a) Photomicrographs of the TGBA* phase of compound **5f** at 171°C (heating). (b) Packing model of the SmA* phase. Tr=tropone ring; Ch=cholesteryl moiety.

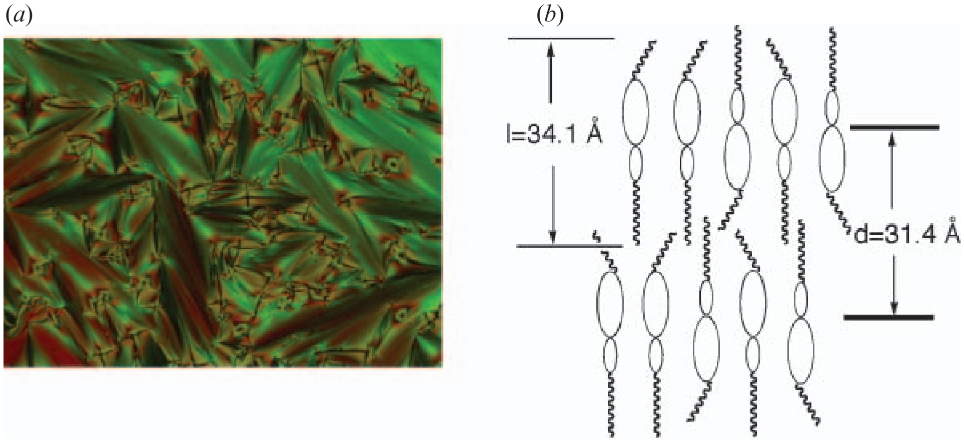
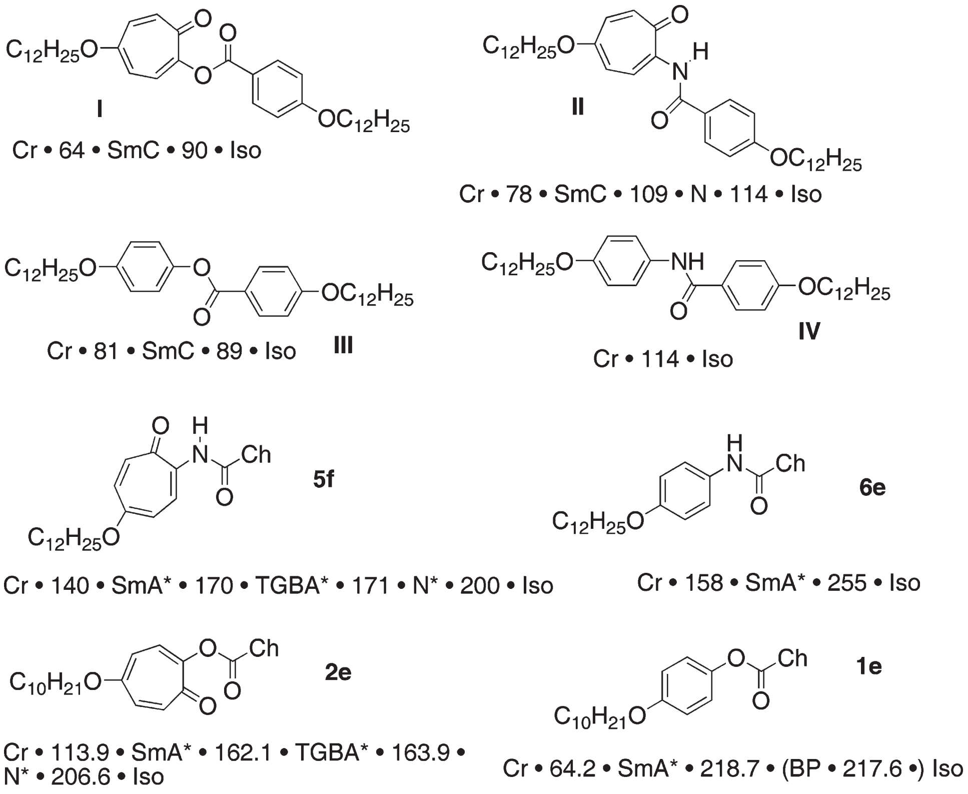


Figure 5. (a) Photomicrographs of the SmA* phase of compound **6b** at 271°C (heating). (b) Packing model of the SmA* phase of **6b**.

model, the core part and the alkyl side chains are well separated than the packing model of troponoid **5** in figure 4b. This is the reason why the thermal stability of the SmA phase of benzenoid amide **6** is higher than that of troponoid amide **5,** as shown in table 3.

2.4. *Comparison of mesomorphic properties of troponoid esters and amides*

Both of troponoid esters (**2** and **4**) and amides (**5**) with a long alkoxy group exhibit SmA*, TGBA* and N* phases. The esters have a lower melting point, a higher transition temperature for the SmA*/TGBA* and TGBA*/N* phases and a lower clearing point than the amides. Previously, we compared the phase transition temperatures of a troponoid ester (**I**) and amide (**II**) (see scheme 2), where the ester had lower thermal stability [10], and discussed the thermal stability of troponoid esters and amides. The ester has a twisted structure, since a single crystallographic analysis of a related troponoid ester, 5-tetradecyloxy-2-(4-dodecylox-



Scheme 2. Structures and transition temperatures of the selected compound.

yaminobenzoyloxy)tropone, indicated that the angle between the tropone part and the benzoyl group is 76.5° [11]. On the other hand, single crystallographic data of a related troponoid amide, 5-butoxy-2-(4-methoxybenzoylamino)tropone, showed that the core structure is almost flat through an intramolecular hydrogen bonding between the tropone carbonyl group and the NH group [11, 12]. Therefore, troponoid amides with a flat core could form more stable layer structures. In the chiral systems, since troponoid amides **5** also have a flat core, amides have stronger lateral interactions, which make the formation of helical structures unfavourable. Since troponoid esters (**2** and **4**) with a twisted core structure do not favour formation of lamellar structures, they form more stable TGBA* phases than troponoid amides.

2.5. *Comparison of mesomorphic properties of troponoids and benzenoids*

We compared the mesomorphic properties of the troponoid esters with those of the benzenoid esters [9]. From table 1, it is obvious that the melting points (Cr–SmA*/N*) of troponoid esters are much higher than those of the corresponding benzenoid esters. The clearing points (SmA*/N*–Iso) could not be compared because some troponoid esters decomposed. The higher melting points of troponoids are due to the presence of the lateral polar carbonyl substituent, which enhances the stability of lateral packing structures.

When the mesomorphic properties are compared of conventional rod-like troponoid and benzenoid liquid crystals with an ester or an amide linking group, both troponoid (**I**) and benzenoid esters (**III**) have similar mesomorphic properties. However, the thermal properties of troponoid amide (**II**) and benzenoid amide (**IV**) are different. Amide **II** is mesomorphic, whereas **IV**, which has a higher melting point, is not. Both compounds, **II** and **IV**, could form hydrogen bonding through the amide group. Although benzenoid amides form intermolecular hydrogen bonding that raises their melting point, troponoid amides have few opportunities to form intermolecular hydrogen bonds since they form intramolecular hydrogen bonds that disturb the intermolecular hydrogen bonding. In amides with a cholesteryl moiety, the situation is the same. Benzenoid amides **6** form intermolecular hydrogen bonding that enhances the thermal stability of the SmA* phase, whereas troponoid amides **5** exhibit less thermally stable SmA* phases because the lateral interaction through intermolecular hydrogen bonding is suppressed. Therefore, troponoid amides form a helical phase such as a TGBA* phase much easier than benzenoid amides.

In the ester derivatives, all benzenoids formed frustrated phases [9]. The lateral interaction of benzenoids is not so strong to hold a lamellar structure because the phenyl group rotates freely around the ester bond. On the other hand, troponoid esters have a more rigid core structure than the benzenoid esters because the tropone ring does not rotate around the ester bond due to [1,9]-sigmatropy. This is the reason why benzenoid esters trend to form frustrated phases.

The positional effects of the lateral carbonyl group of compound **2e** and **3** on the mesomorphic properties are now considered. As shown in table 1, compound **2e** has three types of mesophase, i.e. SmA*, TGBA* and N* phases, whereas compound **3** has only a SmA* phase. In XRD patterns, compounds **2e** and **3** have a broad halo around 5.3 and 3.9 Å, respectively. Compound **2e** has a wider lateral distance than **3**. A single crystallographic study of 5-tetradecyloxy-2-(4-dodecyloxyaminobenzoyloxy)tropone showed that the angle between the tropone ring and the benzoyl group is 76.5° [11]. The core structure is twisted. Compound **2e** with a cholesteryl ester group should have a twisted core structure to form a less stable lamellar structure. These results are consistent with compound **2e** having a weaker lateral packing structure, which makes it possible to form the TGBA* phase, as shown in figure 6.

3. Conclusions

Troponoid esters (**2** and **4**) and amides (**5**) and benzenoid amides (**6**) with cholest-5-ene-3β-carboxylic acid have been prepared and all of them are mesomorphic. Compared with the analogous benzenoid esters (**1**), the troponoid esters have significantly higher melting points, due to the presence of the lateral tropone carbonyl group. The position of the tropone carbonyl group is reflected in the appearance of frustrated phases, as observed in compounds **2e** and **4c**. They have a twisted conformation in their core, which results in a less stable lamellar structure.

Both troponoid esters and amides with a longer alkoxy group at the C-5 position exhibit a TGBA* phase. The TGBA* phase of the troponoid esters showed more stable thermal behavior than the troponoid amides, which have a more stable lamellar structure because of the flat core structure.

The role of the tropone and benzene ring is different between esters and amides. In the case of amides, benzenoid amides form intermolecular hydrogen bonding to increase the thermal stability of the SmA* phase, whereas the amide group of the troponoids form intramolecular hydrogen bonding that suppresses any intermolecular hydrogen bonding. Therefore, the lateral interaction of troponoid

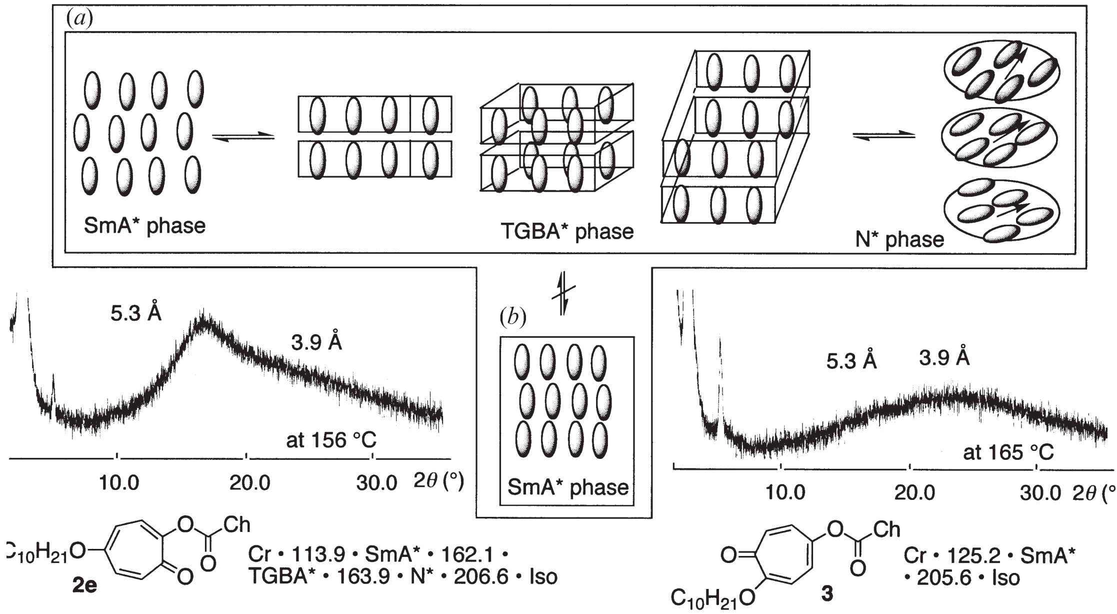


Figure 6. (a) Structures of the SmA*, TGBA* and N* phases of compound **2e**. (b) Structure of the SmA* phase of compound **3** and the wide-angle region of the XRD data of **2e** (left) and **3** (right).

amides is weakened. In esters, troponoids with an acyl group at the C-2 position have a twisted conformation, whereas benzenoid esters have various types of conformation that form less rigid packing structures.

4. Experimental

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University. NMR spectra were measured on JEOL GSX 270H, LA 400, and LA 600 spectrometers in $CDCl_3$; the chemical shifts are expressed in δ units. IR spectra were recorded using a JASCO IR Report 100 spectrometer with KBr disks. The stationary phase for column chromatography was Wako gel C-300 and the eluant was a mixture of ethyl acetate, chloroform and hexane. Transition temperatures were measured using a differential scanning calorimeter (Seiko DSC 200, scanning rate 5°C min^{-1}) and the mesomorphic phase was observed with a polarizing optical microscope (Olympus BHSP BH-2) equipped with a hot stage (Linkam TH-600RMS). X-ray powder diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-K$_\alpha$ radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

4.1. *Synthesis of troponoid esters*

DCC (100 mg, 0.484 mmol) was added to a solution of tropolone (59.1 mg, 0.484 mmol), cholest-5-ene-3β-carboxylic acid (200 mg, 0.484 mmol), DMAP (6.0 mg, 0.0484 mmol) in dichloromethane (20 ml) and *N,N*-dimethylformamide (0.3 ml) while stirring at room temperature and under an argon atmosphere. The reaction mixture was stirred overnight at room temperature, filtered to remove precipitates and the solvent was removed under reduced pressure to give a yellow solid. The crude product was purified by column chromatography (silica gel, hexane:ethyl acetate=4:1), followed by recrystallization (ethanol) to give colourless crystals of **2a**. ^{1}H NMR δ: 0.68 (3H, s), 0.86–2.60 (41H, m), 5.41 (1H, d, J=4.8 Hz), 7.00–7.22 (5H, m). IR (ν_{max}, cm^{-1}): 2952, 1752, 1630, 1603, 1586, 1461, 1380, 1253, 1138, 1041, 964, 837 and 763. Elemental analysis: found, C 80.80, H 9.73%; calculated for $C_{35}H_{50}O_3$, C 81.03, H 9.71%. For **2b**, ^{1}H NMR δ: 0.68 (3H, s), 0.85–2.58 (41H, m), 5.41 (1H, d, J=4.8 Hz), 6.96 (2H, d, J=11.5 Hz), 7.41 (2H, d, J=11.5 Hz). Elemental analysis: found, C 70.27, H 8.22%; calculated for $C_{35}H_{49}BrO_3$, C 70.34, H 8.26%. For **2c**, ^{1}H NMR δ: 0.68 (3H, s), 0.85–2.57 (41H, m), 5.41 (1H, d, J=4.8 Hz), 6.75 (2H, d, J=11.9 Hz), 7.63 (2H, d, J=11.9 Hz). Elemental analysis: found, C 65.38, H 7.65%; calculated for $C_{35}H_{49}IO_3$, C 65.21, H 7.66%. For **2d**, ^{1}H NMR δ: 0.69 (3H, s), 0.86–2.57 (41H, m), 5.41 (1H, d, J=4.8 Hz), 7.19 (2H, d, J=11.1 Hz), 7.34 (2H, d, J=11.1 Hz). Elemental analysis: found, C 79.32, H 9.05, N 2.48%; calculated for $C_{36}H_{49}NO_3$, C 79.52, H 9.08, N 2.58%. For **2e**, ^{1}H NMR δ: 0.68 (3H, s), 0.86–2.57 (60H, m), 3.91 (2H, t, J=6.7 Hz), 5.41 (1H, d, J=4.8 Hz), 6.65 (2H, br), 7.14 (2H, d, J=12.3 Hz). Elemental analysis: found, C 80.05, H 10.41%; calculated for $C_{45}H_{70}O_4$, C 80.07, H 10.45%. For **3**, ^{1}H NMR δ: 0.69 (3H, s), 0.86–2.51 (60H, m), 4.03 (2H, t, J=6.7 Hz), 5.41 (1H, d, J=4.8 Hz), 6.63 (1H, d, J=10.7 Hz), 6.75 (1H, dd, J=10.7, 2.8 Hz), 6.96 (1H, dd, J=13.0, 2.8 Hz), 7.19 (1H, d, J=13.0 Hz). Elemental analysis: found, C 79.97, H 10.46%; calculated for $C_{45}H_{70}O_4$, C 80.07, H 10.45%. Elemental analyses: **4a**, found, C 79.49, H 10.10%, calculated for $C_{41}H_{62}O_4$, C 79.56, H 10.10%; **4b**, found, C 79.57, H 10.28%, calculated for $C_{43}H_{66}O_4$, C 79.83, H 10.28%; **4c**, found, C 80.41, H 10.62%, calculated for $C_{47}H_{74}O_4$, C 80.29, H 10.61%; **4d**, found, C 80.62, H 10.79%, calculated for $C_{49}H_{78}O_4$, C 80.49, H 10.75%; **4e**, found, C 80.68, H 10.89%, calculated for $C_{51}H_{82}O_4$, C 80.68, H 10.89%. The yields of troponoid esters were from 38 to 75%.

4.2. *Synthesis of troponoid amides*

A dry THF solution of 2-amino-5-butoxytropone (38.6 mg, 0.2 mmol), cholest-5-ene-3β-carboxylic acid (103.5 mg, 0.25 mmol), EDC (40 mg, 0.21 mmol) and DMAP (2.5 mg, 0.02 mmol) was stirred at 50°C for 12 h under an argon atmosphere. After the reaction, the reaction mixture was filtered to remove precipitates. The solvent was removed under reduced pressure and the residue was isolated by chromatography on a silica gel column to give **5a**. ^{1}H NMR δ: 0.68 (3H, s), 0.85–2.56 (51H, m), 3.94 (2H, t, J=6.8 Hz), 5.39 (1H, d, J=4.8 Hz), 6.53 (1H, dd, J=11.7, 2.8 Hz), 7.19 (1H, dd, J=13.2, 2.8 Hz), 7.29 (1H, d, J=11.2 Hz), 9.04 (1H, d, J=11.2 Hz), 9.19 (1H, s). m/z 590.4571 (M^++1); calculated for $C_{39}H_{60}NO_3$, 590.4573. For **5b**, elemental analysis: found, C 76.82, H 10.36, N 2.27%; calculated for $C_{41}H_{63}NO_3$, C 79.69, H 10.28, N 2.27%. For **5c**, m/z 645.5119 (M^+); calculated for $C_{43}H_{67}NO_3$, 645.5121. For **5d**, m/z 674.5502 (M^++1); calculated for $C_{45}H_{72}NO_3$, 674.5503. For **5e**, m/z 688.5672 (M^++1); calculated for $C_{46}H_{74}NO_3$, 688.5769. For **5f**, m/z 702.5826 (M^++1); calculated for $C_{47}H_{76}NO_3$, 702.5825. The yields of troponoid amides were from 38 to 71%.

4.3. *Synthesis of benzenoid amides*

A dry THF solution of 4-butoxyaniline (33 mg, 0.25 mmol), cholest-5-ene-3β-carboxylic acid (103.5 mg, 0.25 mmol), EDC (40 mg, 0.2 mmol) and DMAP (2.5 mg, 0.02 mmol) was stirred at 50°C for 12 h under an argon atmosphere. After the reaction, the reaction mixture was filtered. The solvent was removed under reduced pressure and the residue was isolated by chromatography on a silica gel column to give **6a**. ^{1}H NMR δ: 0.69 (3H, s), 0.85–2.56 (48H, m), 3.94 (2H, t, J=6.8 Hz), 5.39 (1H, d, J=4.8 Hz), 6.85 (2H, d, J=8.8 Hz), 7.02 (1H, s), 7.41 (2H, d, J=8.8 Hz). Elemental analysis: found, C 81.49, H 10.68, N 2.29%; calculated for $C_{38}H_{59}NO_2$, C 81.23, H 10.58, N 2.49%. Elemental analyses: **6b**, found, C 81.66, H 11.03, N 2.19%, calculated for $C_{42}H_{67}NO_2$, C 81.63, H 10.93, N 2.27%; **6c**, found, C 81.84, H 11.18, N 1.96%, calculated for $C_{44}H_{71}NO_2$, C 81.80, H 11.08, N 2.17%; **6d**, found, C 81.97, H 11.28, N 1.97%, calculated for $C_{45}H_{73}NO_2$, C 81.88, H 11.15, N 2.12%. For **6e**, m/z 674.5876 (M^++1); calculated for $C_{46}H_{76}NO_2$, 674.5876. The yields of benzenoid amides were from 22 to 56%.

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