Appearance of the Induced Smectic A Phase in the Binary System between Two Troponoid Twins with the Opposite Dipole Moment

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A new troponoid twin system, in which two tropone carbonyl groups direct outside, was prepared, but they were not mesogenic. The binary system between the new twins and the troponoid twins with the two tropone carbonyl groups directed inside, which had a monotropic smectic C phase, showed an induced enantiotropic smectic A phase. From the X-ray diffraction study of the binary systems, a molecular packing model perpendicular to the lamellar planes was proposed, in which the dipole moments of tropone rings were canceled.

It is known that the direction of dipole moments of core parts of liquid crystals is quite important to determine the molecular alignment in a mesophase. As observed in the benzenoid such as three aromatic ring compounds linked by ester groups,[1] the direction of the ester parts affected thermal stability of smectic A phases. They discussed their results from the standpoint of not only the electronic interactions but also the shape of molecules, which played important roles to appearance of the mesophases.

We are using a seven-membered tropolone ring as a core part of liquid crystals because it has a large dipole moment (3.5 D),[2] which would help to form layer structures. In fact, troponoid cores enhanced formation of smectic phases when compared with the corresponding benzenoids.[3]

We recently reported that twin dimers **1**, in which each tropone carbonyl group directs inside, showed a monotropic smectic C phase in small droplets on cooling process while the corresponding benzenoid dimers **2** were not mesogenic.[4] These are consistent of the evidence that monocyclic troponoids[5] were mesogenic while monocyclic benzenoids were not. Due to rapid recrystallization of twins **1**, however, we could not determine the molecular alignment in the mesogenic state of twins **1**. We proposed molecular alignment of the smectic C phase of twins **1** from considering the direction of the dipole moment of twins **1**. In this paper, we report preparation of new twin dimers **3**, in which two tropone carbonyl parts direct outside, to analyze the effect of the direction of dipole moment of troponoids and the mesogenic property of the mixed system of twins **1** and **3**.

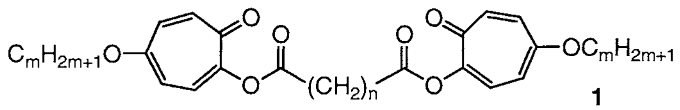
When a tetrahydrofuran solution of 2-alkanoyloxy-5-hydroxytropone (**4**)[6] and alkanoyl dichloride was reacted in the presence of sodium hydride, twins **3**[7] were prepared in 34-74% yields. The transition temperatures and the thermal behavior of the textures were determined using a differential scanning calorimeter and a polarizing microscope equipped with a hot stage. From the thermal behaviors of twins **3**, summarized in Table 1, twin dimers **3** were not mesogenic. The melting points of **3** are higher than those of twin dimers **1**.[4] This is consistent of the result that 2-alkanoyloxy-5-alkoxytropones have lower melting points than 2,5-dialkanoyloxytropones.[6]

In order to investigate mesogenic property of twins **3**, we

Table 1. Transition temperatures of **3**

	m	n	Transition temp. / °C
3a	7	4	Cr • 97.8 • Iso
3b	7	5	Cr • 76.9 • Iso
3c	11	4	Cr • 103.9 • Iso
3d	11	5	Cr • 90.0 • Iso
3e	15	4	Cr • 110.3 • Iso
3f	15	5	Cr • 98.5 • Iso

Cr: crystals, Iso: isotropic liquid.



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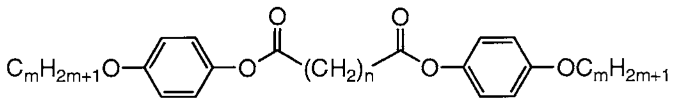

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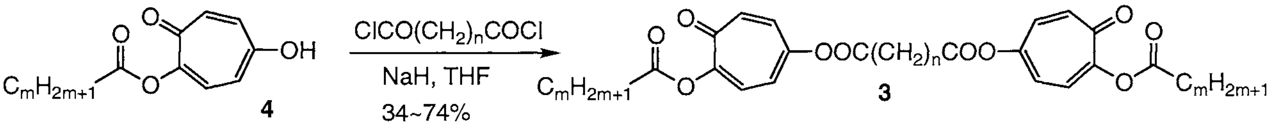

mixed twins **3** and **1**. The results of the binary system are summarized in Table 2. When **1a** (m=16, n=4) and **3e** were mixed in ratios of 10:90 and 20:80, bâtonnets were separated from isotropic liquid and focal-conic fan textures and homeotropic textures were observed. From these observation, the phase should be assigned to smectic A phases. From the ratio from 30:70 to 70:30, an enantiotropic smectic A phase appeared. The clearing points were approximately constant and they were higher than those of pure **1a** and **3e** as shown in Table 2. Furthermore, in the ratio of more than 70% of twin **1a**, a smectic C phase also appeared. Since twin **1a** showed a monotropic smectic C phase and twin **3e** was non-mesogenic, the smectic A phase formed was actually induced by the mixing of these twins.

Table 2. Transition temperatures of the mixtures of **1a** and **3e**[a]

1a	3e	Transition temp. / °C
0	100	Cr • 104 • Iso[b]
10	90	Cr • 100 • Iso[c]
20	80	Cr • 100 • (S_A • 100) • Iso
30	70	Cr • 97 • S_A • 108 • Iso
40	60	Cr • 94 • S_A • 109 • Iso
50	50	Cr • 95 • S_A • 109 • Iso
60	40	Cr • 95 • S_A • 105 • Iso
70	30	Cr • 94 • (S_C • 92) • S_A • 107 • Iso
80	20	Cr • 89 • (S_C • 86) • S_A • 99 • Iso
90	10	Cr • 90 • Iso[d]
100	0	Cr • 93 • Iso[e]

[a] ( ) denotes a monotropic transition. [b] Compound **3e** has the following transition temperature (Cr • 110.3 • Iso) by microscope observation. [c] A S_A phase was observed at 98 °C by microscope observation. [d] A S_C phase was observed at 89 °C by microscope observation. [e] Compound **1a** has the following transition temperature (Cr • 92.7 • (S_C • 82.0) • Iso) by microscope observation.

A layer spacing of the 50:50-mixed sample was determined to be 51 Å by X-ray diffraction measurement at 80 °C where a smectic A phase appeared whereas the layer spacing of the 70:30-mixed sample of twins **1a** and **3e** was 46 Å at 90 °C where a smectic C phase appeared. Since the extended molecular lengths of twins **1a** and **3e** were estimated to be 56 Å and 58 Å from the AM 1 calculation, respectively, the ratio of the layer spacing of the smectic A phase to the extended molecular length is approximately 0.9. In the case of the 70:30-mixed sample, the ratio at 90 °C is approximately 0.8.

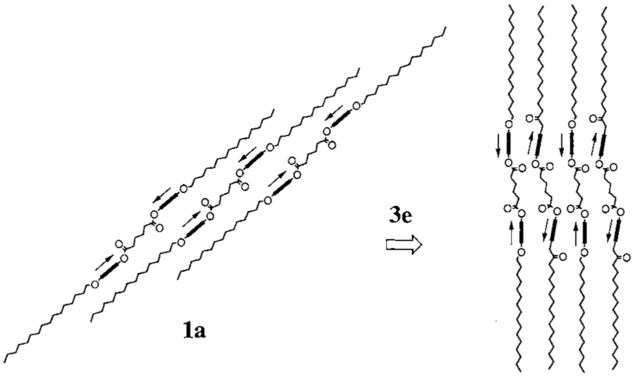

Figure 1. Packing model of the 1:1-mixture of twins **1a** and **3e**. Arrows indicate the direction of dipole moment.

From these data, we proposed the following molecular alignment for the induced smectic A phase in Figure 1, where twin **1a**, which showed a monotropic smectic C phase, would form a tilted layered structure to avoid dipole-dipole repulsion of tropone rings. In the binary system of the 50:50-mixed system, it should be possible to take a parallel arrangement of molecules perpendicular to the lamellar planes, in which the dipole moment of tropone parts would be canceled. This molecular alignment is consistent with the appearance of a smectic A phase.

Thus, the direction of dipole moment of the core should be important to induce mesogenic property. By making the binary phases, a smectic A phase was induced. This result was explained in terms of molecular arrangement of the binary system of twins **1a** and **3e**, in which dipole moments of tropone parts were canceled. In this regard, mesogenic property of a new troponoid twin that has dipole moment directed to the same direction should be interesting.

References and Notes

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7 **3a**: Found: C, 67.64; H, 7.25%. Calcd for $C_{36}H_{46}O_{10}$: C, 67.69; H, 7.26%. **3b**: Found: C, 68.08; H, 7.41%. Calcd for $C_{37}H_{48}O_{10}$: C, 68.04; H, 7.34%. **3c**: Found: C, 70.37; H, 8.32%. Calcd for $C_{44}H_{62}O_{10}$: C, 70.36; H, 8.30%. **3d**: Found: C, 70.65; H, 8.43%. Calcd for $C_{45}H_{64}O_{10}$: C, 70.53; H, 8.39%. **3e**: Found: C, 72.36; H, 9.11%. Calcd for $C_{52}H_{78}O_{10}$: C, 72.24; H, 9.13%. **3f**: Found: C, 72.57; H, 9.19%. Calcd for $C_{53}H_{80}O_{10}$: C, 72.60; H, 9.19%.