

New Twin-Type Troponoid Liquid Crystals with a Smectic C Phase

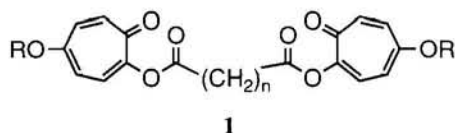
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Twin-type troponoid liquid crystals show a monotropic smectic C phase while the corresponding benzenoids are non-mesogenic. The corresponding troponoid monomers, show a monotropic smectic A phase, could form a head-to-tail alignment. In the twins, molecules have to shift to form a head-to-tail alignment since the dipole moment of the two tropolone parts directs oppositely.

Previously, we have reported that a tropolone ring worked as a superior core of liquid crystals to a benzene ring although it has a wider molecular width than a benzene ring. Even monocyclic troponoids with an ester group at C-2 and an alkoxy group at C-5 show a monotropic smectic A phase¹ while the corresponding benzenoids are not mesogenic. Furthermore, 5-alkylamino-2-(4-alkoxybenzoyloxy)tropolones show a smectic C phase while the corresponding benzenoids are not mesogenic.² It has been observed that the tropone carbonyl group assisted to exhibit the mesogenic properties. In this paper, we describe the preparation and the mesogenic properties of a new twin-type of liquid crystals with two troponoid cores.

When a tetrahydrofuran solution of 5-alkoxytropolone¹ and alkanedioyl dichloride was reacted in the presence of sodium

Table 1. Transition temperatures of **1**

	R	n	Transition temp / °C
1a	C ₆ H ₁₃	3	Cr • 95.9 • Iso
1b	C ₁₂ H ₂₅	4	Cr • 91.0 • (S _C • 71.2 •) Iso
1c		5	Cr • 73.8 • (S _C • 30.1 •) Iso
1d		6	Cr • 72.4 • (S _C • 54.8 •) Iso
1e		7	Cr • 62.4 • (S _C • 22.5 •) Iso
1f		8	Cr • 90.0 • (S _C • 32.5 •) Iso
1g	C ₁₅ H ₃₁	4	Cr • 88.0 • (S _C • 78.7 •) Iso
1h		5	Cr • 83.8 • (S _C • 45.2 •) Iso
1i		6	Cr • 82.1 • (S _C • 64.6 •) Iso
1j		7	Cr • 68.7 • (S _C • 39.2 •) Iso
1k		8	Cr • 71.6 • (S _C • 47.3 •) Iso

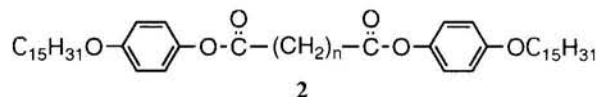
Cr: Crystalline; S_C: Smectic C; Iso: Isotropic; Monotropic transition temperatures were given by reheating process.

hydride, twin dimers **1** were prepared in 22-97% yields.³ The ¹H NMR spectrum of **1** showed a [1,9] sigmatropic rearrangement. The activation free energy of **1a** was determined to be 12.7 kcal/mol from the coalescence temperature at 283 K, which was identical with the value obtained from 2-acetoxy-5-methoxytropolone.⁴

The transition temperatures and the thermal behavior of the texture were determined using a polarizing microscope equipped with a hot stage. The results are summarized in Table 1. Compounds **1** showed a smectic C phase monotropically.

We have already reported that the monomer, 2-acyloxy-5-alkoxytropolone, showed a monotropic smectic A phase.¹ Since tropolone has a dipole moment of 3.5 D, two monomers could form a head-to-tail alignment, which is favored to exhibit a layer structure such as a smectic A phase. In the case of twins **1**, since the dipole moment of the two tropolone parts directs oppositely, we speculated from the core structure of **1** that molecules shifted not only to form a head-to-tail alignment as proposed for the monomer but also to reduce the repulsion of dipole moment of the tropone parts, which allowed to have an intercalated structure.

On the other hand, the corresponding benzenoid twin compounds **2** were not mesogenic as shown in Table 2. They have a higher melting point than **1**. It is a common phenomenon that sigmatropic troponoids have a lower melting point than non-sigmatropic compounds.⁵

Table 2. Transition temperatures of **2**

	n	Transition temp / °C
2a	4	Cr • 99.0 • Iso
2b	6	Cr • 92.3 • Iso
2c	8	Cr • 92.5 • Iso

There observed an even-odd effect of the spacer of **1**. In general, the thermal and mesogenic properties of twin compounds are dependent on the conformation of the central alkylene chain.⁶ In the case of **1** with an even spacer, the mesogenic groups are co-parallel if the spacer is in all-trans conformation. In the case of **1** with an odd spacer, the mesogenic groups are not parallel if the spacer is in all-trans conformation. The latter arrangement could reduce the clearing point.

Compounds **1** with a shorter inner alkylene chain have the higher thermal stability. In the case of **1** with a shorter inner alkylene chain, two troponoid parts are close to form a larger core

part than those with a longer inner alkylene chain, which would be more flexible to reduce the thermal stability.

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References and Notes

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- 2 A. Mori, R. Nimura, and H. Takeshita, *Chem. Lett.*, **1991**, 77; A. Mori, R. Nimura, M. Isobe, and H. Takeshita, *Chem. Lett.*, **1992**, 859.
- 3 Spectral data; **1a**; $^1\text{H-NMR}$ (CDCl_3) δ : 0.91 (6H, t, $J=7.1$ Hz), 1.34 (8H, m), 1.45 (4H, m), 1.80 (4H, m), 2.21 (2H, m), 2.81 (4H, t, $J=7.2$ Hz), 3.92 (4H, t, $J=6.4$ Hz), and 7.17 (4H, d, $J=11.9$ Hz); $^{13}\text{C-NMR}$ (CDCl_3) δ : 14.01, 20.04, 22.55, 25.60, 28.69, 31.42, 32.77, 68.81, 163.01, and 170.80. EA Calcd for $\text{C}_{31}\text{H}_{40}\text{O}_8$: C, 68.87; H, 7.46%. Found: C, 68.80; H, 7.45%. **1b**; EA Calcd for $\text{C}_{44}\text{H}_{66}\text{O}_8$: C, 73.09; H, 9.20%. Found: C, 72.95; H, 9.33%. **1c**; EA Calcd for $\text{C}_{45}\text{H}_{68}\text{O}_8$: C, 73.33; H, 9.30%. Found: C, 72.22; H, 9.31%. **1d**; EA Calcd for $\text{C}_{46}\text{H}_{70}\text{O}_8$: C, 73.56; H, 9.39%. Found: C, 73.40; H, 9.39%. **1e**; EA Calcd for $\text{C}_{47}\text{H}_{72}\text{O}_8$: C, 73.78; H, 9.49%. Found: C, 73.67; H, 9.46%. **1f**; EA Calcd for $\text{C}_{48}\text{H}_{74}\text{O}_8$: C, 74.00; H, 9.57%. Found: C, 73.89; H, 9.55%. **1g**; EA Calcd for $\text{C}_{50}\text{H}_{78}\text{O}_8$: C, 74.40; H, 9.74%. Found: C, 74.67; H, 10.00%. **1h**; EA Calcd for $\text{C}_{51}\text{H}_{80}\text{O}_8$: C, 74.59; H, 9.82%. Found: C, 74.52; H, 9.84%. **1i**; EA Calcd for $\text{C}_{52}\text{H}_{82}\text{O}_8$: C, 74.78; H, 9.90%. Found: C, 74.96; H, 10.19%. **1j**; EA Calcd for $\text{C}_{53}\text{H}_{84}\text{O}_8$: C, 74.96; H, 9.97%. Found: C, 75.13; H, 10.17%. **1k**; EA Calcd for $\text{C}_{54}\text{H}_{86}\text{O}_8$: C, 75.13; H, 10.04%. Found: C, 75.04; H, 9.96%. **2a**; $^1\text{H-NMR}$ (CDCl_3) δ : 0.88 (6H, t, $J=7.1$ Hz), 1.25-1.31 (44H, m), 1.44 (4H, m), 1.77 (4H, m), 1.87 (4H, m), 2.61 (4H, t, $J=7.1$ Hz), 3.92 (4H, t, $J=7.1$ Hz), 6.87 (4H, d, $J=9.0$ Hz), and 6.98 (4H, d, $J=9.0$ Hz). $^{13}\text{C-NMR}$ (CDCl_3) δ : 14.14, 22.70, 24.34, 26.03, 29.26, 29.37, 29.40, 29.58, 29.61, 29.67, 29.68, 29.69, 29.70, 31.93, 33.93, 68.39, 115.01, 122.21, 143.94, 156.81, and 172.18. EA Calcd for $\text{C}_{48}\text{H}_{78}\text{O}_6$: C, 76.75; H, 10.47%. Found: C, 76.72; H, 10.49%. **2b**; EA Calcd for $\text{C}_{50}\text{H}_{82}\text{O}_6$: C, 77.07; H, 10.61%. Found: C, 77.06; H, 10.62%. **2c**; EA Calcd for $\text{C}_{52}\text{H}_{86}\text{O}_6$: C, 77.37; H, 10.74%. Found: C, 77.31; H, 10.75%.
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