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Directional Effects of the Carbonyl Group on the Mesogenic Properties of Twin Troponoids

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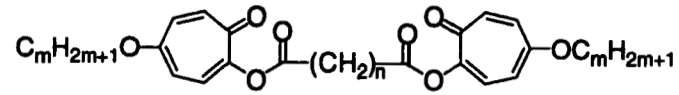
Transition temperatures of four twin types of troponoid liquid crystals, in which the direction of the tropone carbonyl groups and a kind of the spacer were different from each other, were discussed. Symmetrical twin dimers **1**, in which two tropone carbonyl groups direct inside, had monotropic smectic C phases whereas another symmetrical twin dimers **3** were less mesogenic than **1**. Unsymmetrical twin dimers **4** had smectic A phases. Compared their thermal stabilities, unsymmetrical **4** had the highest clearing point when the number of atoms of the inner spacer was identical.

Keywords: Twin-type troponoid liquid crystals; Directional effects of the tropone carbonyl group; X-Ray diffraction study

INTRODUCTION

A lot of twin dimers, in which two mesogenic groups are connected with a flexible spacer, have been synthesized to study their thermal properties [1]. It is well known that the phase behavior of twin type liquid crystals are significantly influenced by the length of the spacer as well as the number of the atoms in the spacer, so-called odd-even nature. Usually, many studies of symmetrical dimers have been reported. The dimers possess higher melting point and clearing temperatures when compared the phase behavior between the dimers and the corresponding monomers.



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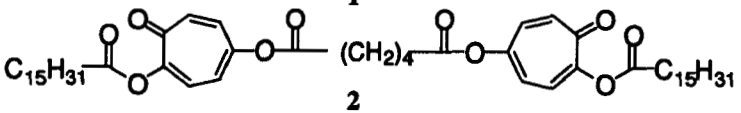

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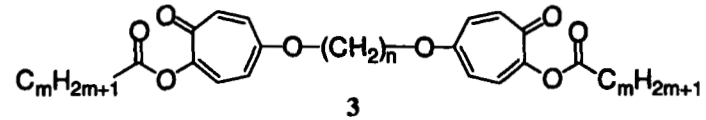

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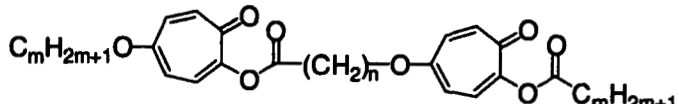

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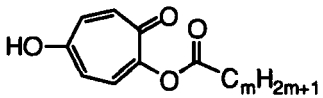
Recently, we have synthesized twin type troponoid liquid crystals (**1**), in which two tropone carbonyl groups direct inside [2]. They had monotropic smectic C phases while the corresponding benzenoids were non-mesogenic and the corresponding monomers showed mono-

tropic smectic A phases [3]. Although twin troponoid, di(4-hexadecanoyloxy-5-oxocycloheptatrienyl) adipate (**2**), in which two tropone carbonyl groups direct outside, was non-mesogenic, the binary system between twins **1** and twin **2** showed an induced enantiotropic smectic A phase [4]. From the X-ray diffraction study of the binary systems, a monolayer molecular packing model was proposed, in which the dipole moments of tropone rings were canceled.

In this paper, we describe the preparation and mesogenic properties of symmetrical **3**, in which two tropone carbonyl groups direct outside and the spacer is a 1,ω-dioxyalkylene group, and unsymmetrical twins **4**, in which one tropone ring directs inside and another one directs outside, to discuss the relationships between direction of the dipole moment of the tropone carbonyl group and mesogenic properties.

RESULTS AND DISCUSSION

Symmetrical twins **3** were prepared from the reaction of 2-alkanoyloxy-5-hydroxytropones (**5**) [5] and 1,ω-dibromoalkane. Similarly, unsymmetrical twins **4** were prepared from the reaction of **5** and 5-alkoxy-2-(ω-bromoalkanoyloxy)tropones (**6**), which was synthesized from 5-alkoxytropolones and ω-bromoalkanoyl chloride. The transition temperatures and the thermal behavior of the texture were determined using a polarizing microscope equipped with a hot stage and are summarized in Figure 1.



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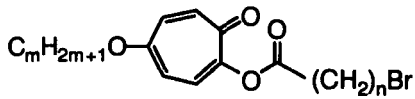

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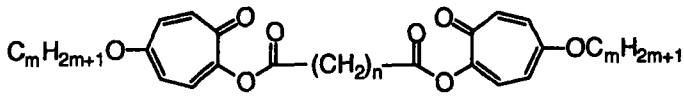
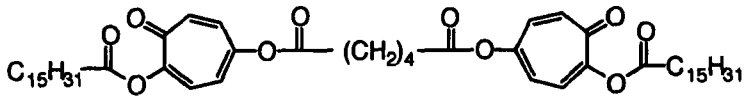


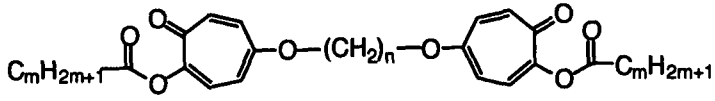
1a (m=15, n=4) Cr • 88.0 • (S_C • 78.7 •) Iso

1b (m=15, n=5) Cr • 83.8 • (S_C • 45.2 •) Iso

1c (m=16, n=4) Cr • 92.7 • (S_C • 82.0 •) Iso



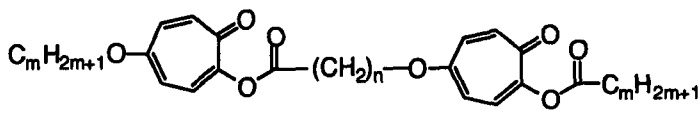
2 Cr • 110.3 • Iso



3a (m=15, n=6) Cr • 93.6 • Iso

3b (m=17, n=4) Cr • 106.3 • (S_C • 97.1 •) Iso

3c (m=17, n=6) Cr • 98.7 • Iso



4a (m=13, n=4) Cr • 94.2 • (S_A • 92.0 •) Iso

4b (m=15, n=4) Cr • 94.4 • S_A • 95.9 • Iso

4c (m=15, n=5) Cr • 118.6 • (S_A • 100.7 •) Iso

FIGURE 1. Transition temperatures of the troponoid twins

As mentioned above, twin dimers **1** showed monotropic smectic C phases [4]. In the case of twin dimers **3**, they were less mesogenic than **1**. Twin dimer **3b** which has long alkyl chains and a short alkylene chain, however, showed monotropic smectic C phases. Twin dimers **4** showed smectic A phases.

In these troponoid twins, when compared their thermal stabilities among **1a**, **3a**, and **4c**, in which the number of atoms of the inner spacer was fixed to 8, unsymmetrical twin dimer **4c** had the highest clearing points. In symmetrical troponoid twins **1** and **3**, the dipole moments of two tropone carbonyl groups directed oppositely, which means that molecules could not form a perpendicular molecular arrangement. Twin dimers **4**, however, could form head-to-tail layer structure to cancel dipole moment of tropone rings.

CONCLUSION

Symmetrical twin troponoids **1** showed monotropic smectic C phases to form layer structure in which molecules would tilt in order to relieve this dipole repulsion. In contrast, twin troponoids **4** could form a head-to-tail arrangement in order to cancel dipole moment of tropone carbonyl groups. Thus, the direction of the tropone carbonyl group was critical to exhibit mesophases.

Furthermore, the contrast of the lengths between the side chains and the flexible spacer was quite important to induce stable mesogenic state as observed in **3b**, which showed monotropic smectic C phases whereas other homologues were not mesogenic.

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