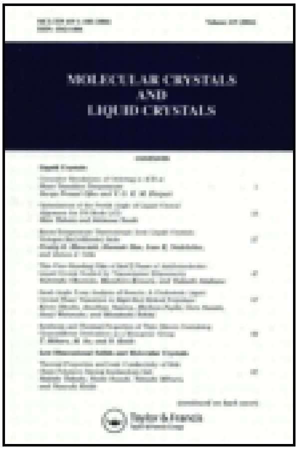

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Troponoid Twin Dimers with Four Rings: Synthesis and Mesomorphic Properties

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TROPONOID TWIN DIMERS WITH FOUR RINGS: SYNTHESIS AND MESOMORPHIC PROPERTIES

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Twin-type troponoids with two benzene and two tropone rings were prepared. They showed nematic phases when the inner and the side chains are short while smectic A phases appear when the inner chain becomes long. Twins with long side chains and a short inner chain had smectic C phases. From X-ray diffraction study, molecular packing models are proposed. The corresponding benzenoid twins showed nematic and smectic C phases with higher thermal stability than the troponoids.

Keywords: dipole-dipole interaction; packing models; twin-type troponoid and benzenoid liquid crystals; X-ray diffraction study

INTRODUCTION

Recently we have prepared troponoid twin dimers with two tropone rings; an unsymmetrical dimer, in which two carbonyl groups direct to the same direction, had a monotropic smectic A phase [1,2]. A symmetrical dimer, in which two tropone carbonyl groups direct inside, had a monotropic smectic C phase [3] whereas another symmetrical dimer, whose troponoid rings direct outside, was not mesomorphic. Among troponoid twins, the

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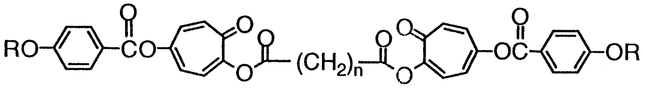
unsymmetrical dimer had the highest clearing point when the number of atoms of the inner spacer was fixed. When symmetrical twins with monotropic smetic C phases and the other non-mesomorphic symmetrical twins were mixed, smectic A phases were induced with higher transition temperatures than the pure twins [1,4].

In order to determine the layer structure of the smectic phases of twin dimers, we prepared thermally stable troponoid and benzenoid twin dimers with four rings, which showed enantiotropic smectic phases when side chains were long. In this paper, we will report the results.



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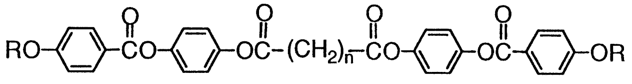

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RESULTS AND DISCUSSION

Troponoid twin dimers (**1**) were prepared from the reaction of 5-(4-alkoxybenzoyloxy)tropolone [5] and alkanedioyl dichloride in tetrahydrofuran (**THF**) in the presence of sodium hydride (NaH) in 24–67% yields [6]. Similarly, a **THF** solution of 4-hydroxyphenyl 4-alkoxybenzoate and alkanedioyl dichloride was stirred at room temperature to give benzenoid twins (**2**). The transition temperatures and the thermal behavior of the texture were determined using a polarizing microscope equipped with a hot stage as well as X-ray diffraction study. The results are summarized in Table 1.

When an inner alkylene and outer alkyl chains of **1** were short, they had nematic phases. While an inner chain became long, smectic A phases with fan and homeotropic textures began to appear. Twins **1** with the longer outer chains and the shorter inner chain showed smectic C phases with schlieren and fan textures. Furthermore, an odd-even effect on the alkylene chain was observed: the thermal; stability of the mesophases decreased in **1** with an odd alkylene chain. Thus, mesogenic properties are dependent on the inner and the outer alkyl chain lengths.

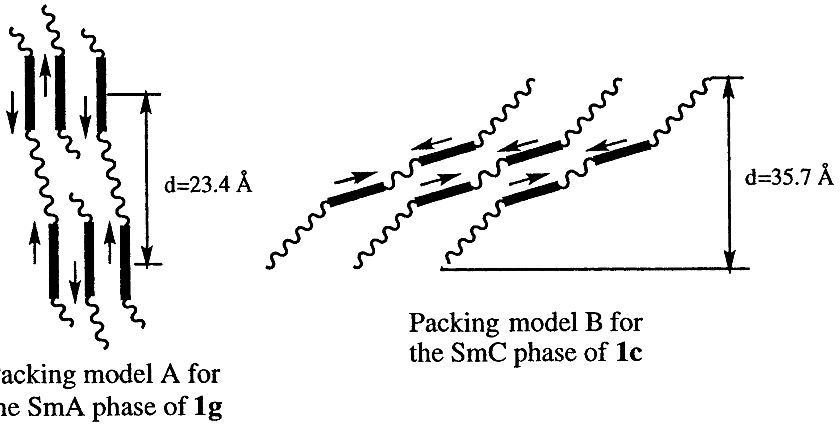
X-ray diffraction study of twin **1g** at 141°C showed that the smectic layer spacing (d) is 23.36 Å. The layer spacing was independent on the temperatures since the layer spacing at 131°C is 23.43 Å. The calculated molecular length of **1g** is 46.3 Å [7]. On the other hand, X-diffraction study of twin **1g** with longer outer and shorter inner chains indicated that the layer spacing is 35.7 Å at 110°C. The calculated molecular length is 64.1 Å [7].

TABLE 1 Transition Temperatures of **1**

	R	n	Transition temp./°C
1a	C_4H_9	4	Cr ● 145.0 ● N ● 174.6 ● I
1b	$C_{10}H_{21}$	4	Cr ● 120 ● SmC ● 142 ● N ● 155 ● I
1c	$C_{14}H_{29}$	4	Cr ● 109.5 ● SmC ● 160.1 ● I
1d	C_4H_9	5	Cr ● 130.9 ● (N ● 126.8 ●) I
1e	C_4H_9	6	Cr ● 159.3 ● (SmA ● 105.8 ●) N ● 165.1 ● I
1f	C_4H_9	7	Cr ● 126.0 ● (SmA ● 92.3 ●) N ● 127.8 ● I
1g	C_4H_9	8	Cr ● 129.6 ● SmA ● 141.2 ● N ● 147.2 ● I
1h	$C_{14}H_{29}$	8	Cr ● 99.1 ● SmC ● 119.6 ● I

Cr: Crystalline, N: Nematic, SmC: Smectic C, SmA: Smectic A, I: Isotropic. Monotropic transition temperatures were given by reheating process.

Taking the direction of the dipole moment of the tropone part into account, the molecular model A for smectic A phases and model B for smectic C phases are proposed in Figure 1. When the inner chain is longer and the side chains are shorter, the molecular model A, in which tropone rings are in head-to-tail arrangement to cancel dipole-dipole interaction, could become favored to exhibit smectic A phases. While the length of side chains is longer, it would become difficult to have model A because of repulsion between side chains. This is a reason why twins **1** with longer outer chains did not show smectic A phases. In the case of **1c**, molecules tilted to avoid dipole-dipole repulsion. When compared the thermal stability of the



Packing model A for the SmA phase of 1g

Packing model B for the SmC phase of 1c

FIGURE 1 Molecular packing models. The arrows show the direction of the dipole moment of the troponoid core.

TABLE 2 Transition Temperatures of **2**

	R	n	Transition temp./°C
2a	C_4H_9	4	Cr ● 148 ● N ● 180 ● I
2b	$C_{10}H_{21}$	4	Cr ● 134 ● SmC ● 178 ● N ● 183 ● I
2c	$C_{14}H_{29}$	4	Cr ● 122 ● SmC ● 183 ● I
2d	C_4H_9	5	Cr ● 139 ● SmC ● 122 ● I
2e	C_4H_9	6	Cr ● 151 ● N ● 161 ● I
2f	C_4H_9	7	Cr ● 138 ● N ● 160 ● I[a]

[a] See reference [11].

smectic C phase between **1c** and **1h** with two tetradecyl groups as the outer chains, the latter with a long spacer had lower thermal stability. This is parallel to the twin-type troponoid liquid crystals with two tropone rings [1].

It is known that increasing the spacer length promotes nematic behavior for dimeric liquid crystals [8]. This observation has been attributed to the increase in the overall molecular flexibility. In the α, ω-bis (4-n-alkylaniline-benzylidene-4′-oxy)alkanes, it was observed that higher members exhibit purely nematic behavior [9], which is reverse tendency observed in monomeric mesogens. In the case of troponoid twins, the shorter alkylene members exhibited nematic phases whereas the longer ones did smectic ones. This observation is in accord with the general result in monomeric mesogens [10].

The corresponding benzenoid twin compounds (**2**) showed a nematic phase as shown in Table 2 when the inner and outer alkyl chain were relatively short [11]. It would be explained that the tropone carbonyl group played as a lateral polar substituent to enhance the smectic property and to reduce the thermal stability of the nematic phase when compared with those of the benzenoids as observed in 2,5-(4-alkoxybenzoyloxy)tropones [5]. However, when the outer side chain becomes long, smectic C phases appeared with higher thermal stability than the troponoids and the thermal stability of the smectic C phases of the benzenoid twin increased. X-ray diffraction study of **2c** showed that the layer spacing is 41.2 Å. The calculated molecular length is 69.0 Å.

CONCLUSION

Two types of twin dimers were prepared. Packing models A and B were proposed for smectic A and C phases of twins **1**. When thermal stability of mesophases was compared between **1** and **2**, the latter has better results in both nematic and smectic phases.

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