Synthesis and Mesogenic Properties of New Non-Sigmatropic, Monocyclic Troponoids, 5-Acyloxy-2-alkoxytropones

Akira Mori,* Shinji Takematsu,† Masahiro Isobe,† and Hitoshi Takeshita*
Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816
†*Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816*

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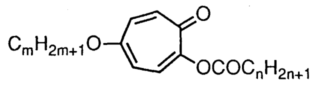
A series of newly-prepared non-sigmatropic 5-acyloxy-2-alkoxytropones showed virtual S_A-C transition temperatures as determined by extrapolation of the binary phase diagram. This is an example of the genuine monocyclic liquid crystals.

Recently, we have reported that monocyclic 2-acyloxy-5-alkoxytropones (**1**) showed a monotropic smectic A phase and that the acyloxy group at C-2 played an important role to exhibit mesophases.[1] We have observed in the ^{13}C CPMAS that the benzoyl group at C-2 of 2-(4-dodecyloxybenzoyloxy)-5-dodecyloxytropone migrated to the carbonyl group in the mesophase.[1,2] This migration could induce the linearity and the planarity of the molecule to assist the compounds mesogenic.[3] In this paper, we report the synthesis and the mesogenic property of non-sigmatropic 5-acyloxy-2-alkoxytropones (**2**).

When 5-hydroxytropolone (**3**) was mixed with pivaloyl chloride in the presence of sodium hydride, 5-pivaloyloxytropolone (**4**) was obtained in 65% yield. Alkylation of **4** with alkyl iodides gave 2-alkoxy-5-pivaloyloxytropones (**5**), whose hydrolysis with an aqueous KOH solution gave 2-alkoxy-5-hydroxytropones (**6**) in 70-90% yields. Finally, **6** was reacted with various acyl chlorides to give **2** in 40-70% yields. The phase transition temperatures were determined using a differential scanning calorimeter and a microscopic observation.

During a rapid cooling process of **2**, a mesophase was



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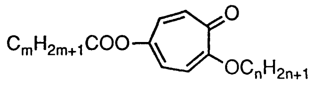

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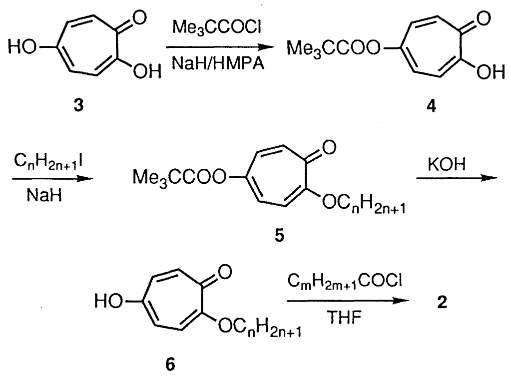


Scheme 1

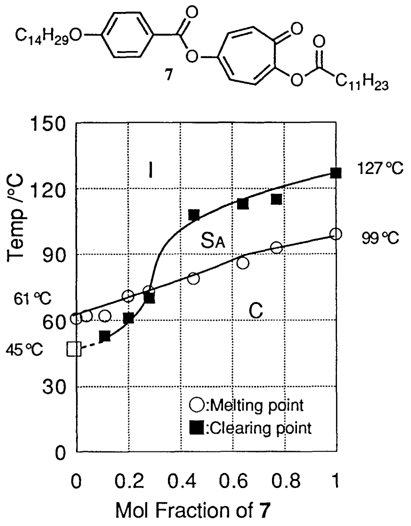
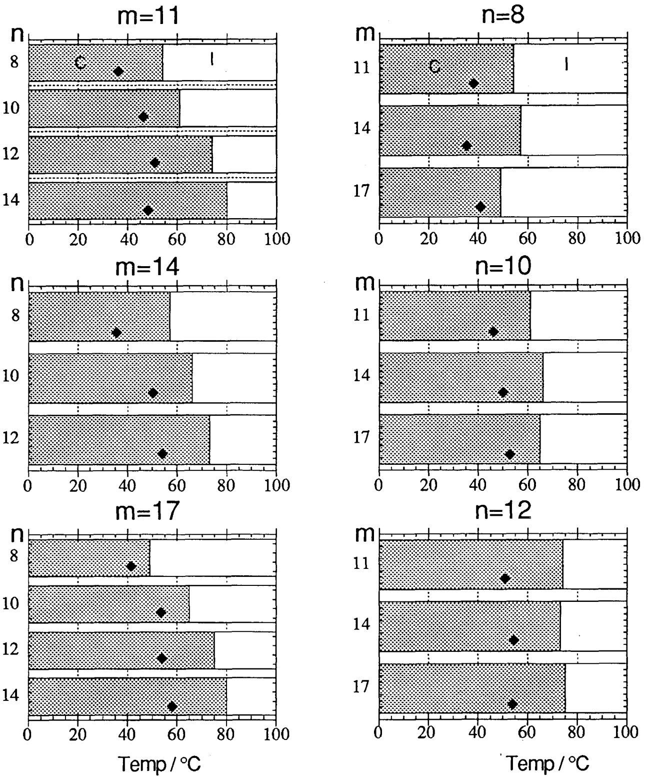
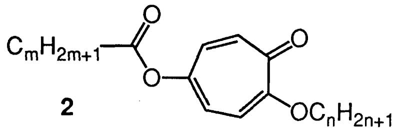


Figure 1. Binary Phase Diagram of **2b** and **7** (I: Isotropic liquid, S_A: Smectic A phase, C: Crystals).



◆: Transition temperature determined by extrapolation.

Figure 2. Effect of the Alkyl Chain Length on the Transition Temperature of **2**.



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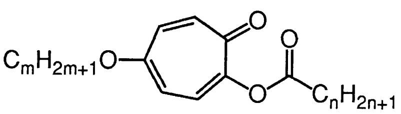

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Table 1. Transition Temperatures (°C) of **1** (right) and **2** (left)

	m	n	C		S_A		I	m	n	C		S_A		I
a	11	8	•	54	•	(38)[a]	•	12	9	•	48	•	(46)	•
b	11	10	•	61	•	(45)	•	12	11	•	58	•	(45)	•
c	11	12	•	74	•	(50)	•	12	13	•	63	•	(51)	•
d	11	14	•	80	•	(47)	•	15	7	•	41	•	(39)	•
e	14	8	•	57	•	(36)	•	15	9	•	48	•	(47)	•
f	14	10	•	66	•	(50)	•	15	11	•	60	•	(52)	•
g	14	12	•	73	•	(54)	•	18	7	•	49	•	(39)	•
h	17	8	•	49	•	(41)	•	18	9	•	53	•	(46)	•
i	17	10	•	65	•	(53)	•	18	11	•	60	•	(52)	•
j	17	12	•	75	•	(54)	•							
k	17	14	•	80	•	(57)	•							

[a] Transition temperatures determined by extrapolation.

momentarily observed. Then, the virtual S_A-C transition temperatures were determined by extrapolation of the binary phase diagram between **2** and 2-dodecanoyloxy-5-(4-tetradecyloxybenzoyloxy)tropone (**7**) with an enantiotropic S_A phase.[4] The diagram in Figure 1 indicates that **2b** intrinsically possesses a S_A-C transition at 45 °C.

Table 1 summarizes the virtual S_A-C transition temperatures together with the transition temperatures of the monotropic S_A of **1**.[1,2] The melting point of **2** was higher than that of **1**. The ester group at C-5 of **2** made the melting point higher. In another words, the acyl group of **1** made the molecules linear and the melting point low since both carbonyl groups of **1** are concerned in the sigmatropic rearrangement to make the intermolecular interaction weaker.

Figure 2 shows the effect of the alkyl chain length on the temperature of the virtual S_A-C transition. The chain length of C_nH_{2n+1} at C-2 was more effective than that of C_mH_{2m+1} on both the phase transition temperature and the melting point.

Compared with the mesogenic properties of **1** and **2**, it is confirmed that the ester group at C-2 of **1** assisted the appearance of the mesophase through the sigmatropic rearrangement.[1-3,5] Furthermore, a corresponding benzenoid, 4-decyloxyphenyl dodecanoate, was non-mesogenic.

Thus, the tropone carbonyl group played the decisive role as a lateral polar group. In addition, the present result constitutes a genuine example of monocyclic liquid crystals; the previous 2-acyloxytropones (**1**) might be "bicyclic" if one considers the transition geometry of the sigmatropy as cyclic.

References and Notes

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