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## Liquid Crystals

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## Intermolecular hydrogen bonding as an aid to the preferential exhibition of the smectic C phase in troponoid liquid crystals

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2-(4-Alkoxybenzoyloxy)-5-alkylaminotropone and 5-alkoxy-2-(4-alkylamino-benzoyloxy)troponoid liquid crystals showed the smectic C phase exclusively. Variable temperature FT-IR spectra indicated that intermolecular hydrogen bonding between the NH and troponoid C=O groups assisted the appearance of the mesophase. 4-Alkoxyphenyl 4-alkylaminobenzoates were non-mesogenic.

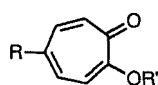
### 1. Introduction

The core structure of rod-like liquid crystals generally consists of six-membered rings, i.e. benzene or cyclohexane rings. It has been known that a wide ring is less favourable as a core. A troponoid molecule has a carbonyl group and the molecular width is wider than that of a benzenoid molecule. Recently, we reported the role of the carbonyl group on the appearance of the mesophase in rod-like monocyclic liquid crystals (1) [1] and flexible 2-benzoyloxytroponoid derivatives (2) [2]. In the former, the carbonyl group acts as an acceptor of acyl group migration to form a pseudo ring in the transition state and in the latter as a lateral polar substituent to attract molecules.

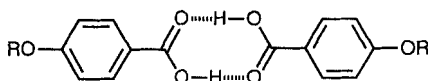
It is known that molecular interactions play an important role not only on the appearance but also the thermal stability of the mesophase. Hydrogen bonding is a typical molecular interaction which orders molecules, but it has a negative factor with respect to the appearance of the mesophase since it raises the melting point above the mesophase-isotropic transition temperature [3]. Hydrogen bonding enables the formation of a mesophase by forming stable dimers in aromatic acids (3) [4] and monosaccharides (4) [5]. Recently, Kato *et al.* reported new liquid-crystalline complexes between two different components [6]. Thus, hydrogen bonding enhances the appearance of a mesophase in certain instances.

In this paper we report the preparation of new troponoid liquid crystals, 2-(4-alkoxybenzoyloxy)-5-alkylaminotropone (5) [7] and 5-alkoxy-2-(4-alkylamino-benzoyloxy)troponoid (6) [8], which could be controlled to show exclusively a smectic C phase due to intermolecular hydrogen bonding between an amino hydrogen atom and the troponoid carbonyl group.

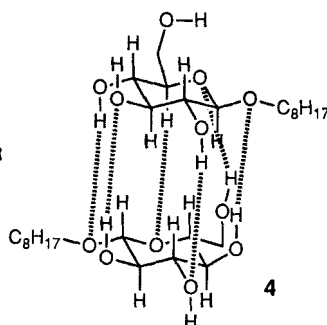
\*Author for correspondence.



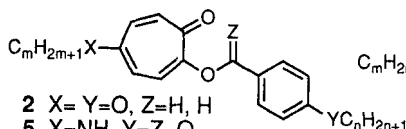
- 1**  $R=OC_mH_{2m+1}$ ,  $R'=COC_nH_{2n+1}$   
**7**  $R=NH_2$ ,  $R'=H$   
**8**  $R=OH$ ,  $R'=H$   
**9**  $R=OC_mH_{2m+1}$ ,  $R'=H$



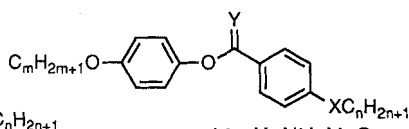
3



4



- 2**  $X=Y=O$ ,  $Z=H$ ,  $H$   
**5**  $X=NH$ ,  $Y=Z=O$   
**6**  $X=Z=O$ ,  $Y=NH$   
**10**  $X=Y=Z=O$



- 11**  $X=NH$ ,  $Y=O$   
**12**  $X=O$ ,  $Y=H$ ,  $H$

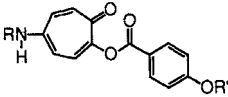
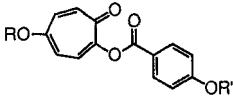
## 2. Experimental

Compound **5** was prepared by monoalkylation of 5-aminotropolone (**7**) at the C-5 position and a subsequent benzylation. Compound **6** was prepared by means of monoalkylation of 5-hydroxytropolone (**8**) at the C-5 position and subsequent benzylation of 5-alkoxytropolones (**9**) with 4-alkylaminobenzoil chloride. The measurement of the phase transition temperatures was carried out using a differential scanning calorimeter (DSC) and the mesomorphic phase was observed by a polarizing microscope equipped with a hot stage. The results are summarized in tables 1 and 2 together with those of 5-alkoxy-2-(4-alkoxybenzoyloxy)tropolones **10** [1] and those of the corresponding benzene derivatives, 4-alkoxyphenyl 4-alkylaminobenzoates (**11**), which were prepared similarly from hydroquinone.

## 3. Results and discussion

When the mesophases of **5** and **10** were compared, the latter showed nematic, smectic A and smectic C phases whereas the former showed a smectic C phase exclusively when mesogenic. It is noteworthy that the different properties arose only by changing the heteroatom at the C-5 position of the tropone ring from an oxygen to a nitrogen atom. Compound **6** showed a smectic C schlieren texture, whereas the corresponding compound **11** was non-mesogenic. The mesogenic property was dependent on the core structure, i.e. the presence of the tropone carbonyl group is essential for mesogenicity. It was expected that the tropone C=O group with a permanent dipole moment stabilizes the smectic phase by increasing the attractive dispersion force [9] between molecules as has been observed in **2** and the benzene derivative, **12**. The former was mesogenic, but the latter was not [2]. In addition,

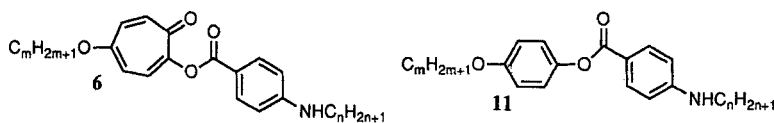
Table 1. Transition temperatures ( $^{\circ}\text{C}$ ) and enthalpy changes ( $\Delta H/\text{kJ mol}^{-1}$ ), in brackets, of **5** and **10**.

	<i>R</i>	<i>R'</i>	<b>5</b>	<b>10</b>
<b>a</b>	$\text{C}_6\text{H}_{13}$	$\text{C}_{12}\text{H}_{25}$	$\text{C} \xrightleftharpoons[96(23.4)]{102(22.9)} \text{I}$	$\text{C} \xrightleftharpoons[54(0.7)]{58(48.3)} \text{N} \xrightleftharpoons[66(2.8)]{66(1.7)} \text{I}$ $\swarrow \text{S}_C$
<b>b</b>	$\text{C}_8\text{H}_{17}$	$\text{C}_{12}\text{H}_{25}$	$\text{C} \xrightleftharpoons[90(24.6)]{100(23.0)} \text{I}$	$\text{C} \xrightleftharpoons[76(5.6)]{67(34.8)} \text{S}_C \xrightleftharpoons[76(4.3)]{76(5.6)} \text{I}$
<b>c</b>	$\text{C}_{11}\text{H}_{23}$	$\text{CH}_3$	$\text{C} \xrightleftharpoons[120(43.6)]{137(41.5)} \text{I}$	$\text{C} \xrightleftharpoons[45(1.7)]{66(53.9)} \text{N} \xrightleftharpoons[45(1.7)]{66(53.9)} \text{I}$
<b>d</b>	$\text{C}_{11}\text{H}_{23}$	$\text{C}_{12}\text{H}_{25}$	$\text{C} \xrightleftharpoons[88 \swarrow \text{S}_C \nwarrow 91]{94(24.4)} \text{I}$	$\text{C} \xrightleftharpoons[85(6.3)]{51(54.4)} \text{S}_C \xrightleftharpoons[85(6.3)]{85(7.0)} \text{I}$
<b>e</b>	$\text{C}_{12}\text{H}_{25}$	$\text{CH}_3$	$\text{C} \xrightleftharpoons[111(46.6)]{133(45.5)} \text{I}$	$\text{C} \xrightleftharpoons[44(34.7)]{71(42.3)} \text{N} \xrightleftharpoons[50(1.7)]{71(42.3)} \text{I}$
<b>f</b>	$\text{C}_{12}\text{H}_{25}$	$\text{C}_4\text{H}_9$	$\text{C} \xrightleftharpoons[87(24.0)]{95(22.6)} \text{I}$	$\text{C} \xrightleftharpoons[63 \swarrow \text{S}_C \nwarrow]{64(24.3)} \text{S}_A \xrightleftharpoons[70(5.4)]{70(4.6)} \text{I}$
<b>g</b>	$\text{C}_{12}\text{H}_{25}$	$\text{C}_{12}\text{H}_{25}$	$\text{C} \xrightleftharpoons[88(14.8) \swarrow \text{S}_C \nwarrow 95(8.3)]{96(25.2)} \text{I}$	$\text{C} \xrightleftharpoons[90(10.2)]{64(69.0)} \text{S}_C \xrightleftharpoons[90(10.2)]{90(9.8)} \text{I}$
<b>h</b>	$\text{C}_{14}\text{H}_{29}$	$\text{C}_{12}\text{H}_{25}$	$\text{C} \xrightleftharpoons[87(24.9)]{99(18.3)} \text{S}_C \xrightleftharpoons[103(17.9)]{104(16.5)} \text{I}$	$\text{C} \xrightleftharpoons[95(14.1)]{73(96.5)} \text{S}_C \xrightleftharpoons[95(14.1)]{95(14.1)} \text{I}$
<b>i</b>	$\text{C}_{18}\text{H}_{37}$	$\text{C}_{12}\text{H}_{25}$	$\text{C} \xrightleftharpoons[86(29.6)]{98(14.9)} \text{S}_C \xrightleftharpoons[104(14.8)]{105(9.2)} \text{I}$	$\text{C} \xrightleftharpoons[95(16.0)]{80(119.6)} \text{S}_C \xrightleftharpoons[95(16.0)]{95(16.3)} \text{I}$

compound **6** have a [1, 9] sigmatropic system, which caused them to be mesogenic [1], while the benzenoid **11** has no such system.

In figure 1 are shown the temperature dependent FT-IR spectra of 5-(dodecylamino)-2-(4-dodecyloxybenzoyloxy)troponone (**5g**), which exhibited a monotropic smectic C phase. The large spectral changes were observed in the NH absorption around  $3400\text{ cm}^{-1}$ , in the ester C=O absorption around  $1700\text{--}1730\text{ cm}^{-1}$ , and in the troponone C=O and C=C absorptions around  $1500\text{--}1600\text{ cm}^{-1}$ . On the other hand, the C-H stretching absorption around  $2800\text{--}3000\text{ cm}^{-1}$  and the C=C absorption of the benzene ring around  $1620\text{ cm}^{-1}$  changed slightly. From these observations, intermolecular hydrogen bondings between the NH group and the ester and the troponone C=O groups were predicted. The absorption of the NH stretching appeared at  $3387\text{ cm}^{-1}$  in the crystalline state and that in the liquid-crystalline state at

Table 2. Transition temperatures ( $^{\circ}\text{C}$ ) and enthalpy changes ( $\Delta H/\text{kJ mol}^{-1}$ ), in brackets, of **6** and **11**.

	<i>m</i>	<i>n</i>	<b>6</b>	<b>11</b>
<b>a</b>	12	8	$\text{C} \xrightleftharpoons[84]{108(27)} \text{S}_\text{C} \xrightleftharpoons[90]{90} \text{I}$	$\text{C} \xrightleftharpoons[120(54)]{124(55)} \text{I}$
<b>b</b>	12	10	$\text{C} \xrightleftharpoons[90]{112(51)} \text{S}_\text{C} \xrightleftharpoons[98]{98} \text{I}$	$\text{C} \xrightleftharpoons[108(30)]{115(33)} \text{I}$
<b>c</b>	12	12	$\text{C} \xrightleftharpoons[101]{108(50)} \text{S}_\text{C} \xrightleftharpoons[108]{108} \text{I}$	$\text{C} \xrightleftharpoons[110(45)]{116(48)} \text{I}$
<b>d</b>	14	12	$\text{C} \xrightleftharpoons[91(37)]{109} \text{S}_\text{C} \xrightleftharpoons[106(9)]{115} \text{I}$	$\text{C} \xrightleftharpoons[109(52)]{115(60)} \text{I}$
<b>e</b>	18	12	$\text{C} \xrightleftharpoons[95(38)]{108} \text{S}_\text{C} \xrightleftharpoons[111(11)]{111} \text{I}$	$\text{C} \xrightleftharpoons[109(72)]{115(70)} \text{I}$
<b>f</b>	18	18	$\text{C} \xrightleftharpoons[93]{111(130)} \text{S}_\text{C} \xrightleftharpoons[111]{111} \text{I}$	$\text{C} \xrightleftharpoons[98(16)]{106(12)} \text{C}_2 \xrightleftharpoons[106(72)]{113(51)} \text{I}$

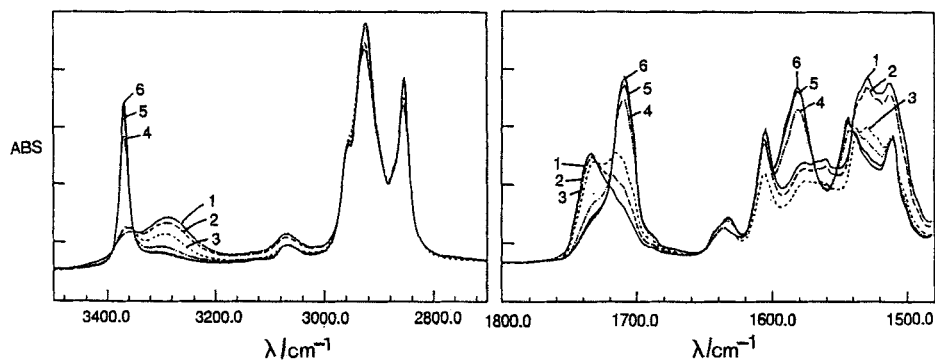
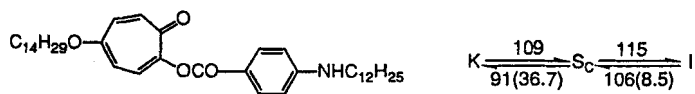
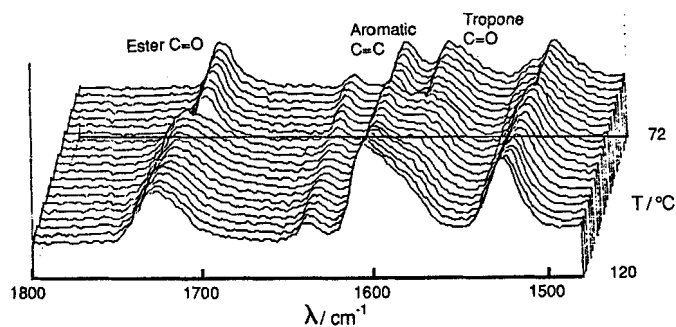
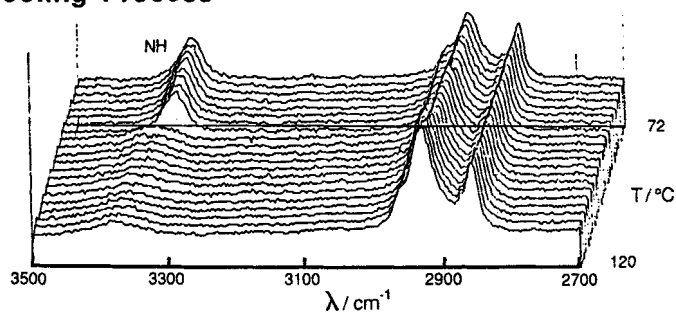


Figure 1. Variable temperature FT-IR spectra of 5-(dodecyloxy)-2-(4-dodecylaminophenyl)troponone (**5g**). Curve 1 at  $100^{\circ}\text{C}$ ; Curve 2 at  $95^{\circ}\text{C}$ ; Curve 3 at  $90^{\circ}\text{C}$ ; Curve 4 at  $85^{\circ}\text{C}$ ; Curve 5 at  $80^{\circ}\text{C}$ ; Curve 6 at  $75^{\circ}\text{C}$ .



Cooling Process



Heating Process

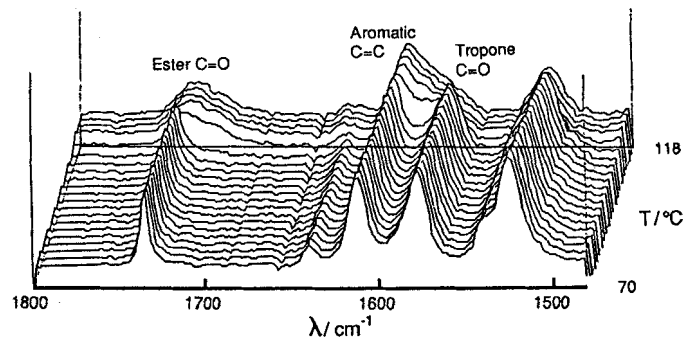
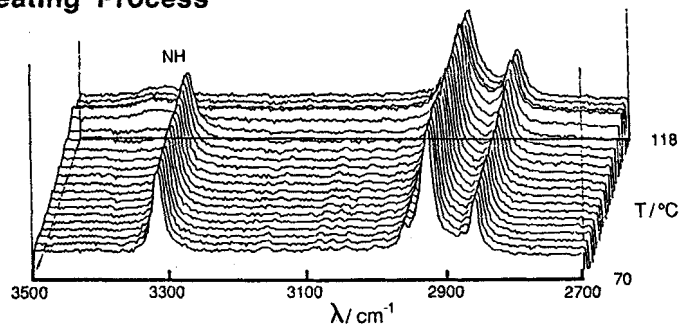


Figure 2. Variable temperature FT-IR spectra of **6d**. Cooling process (upper) and heating process (lower).

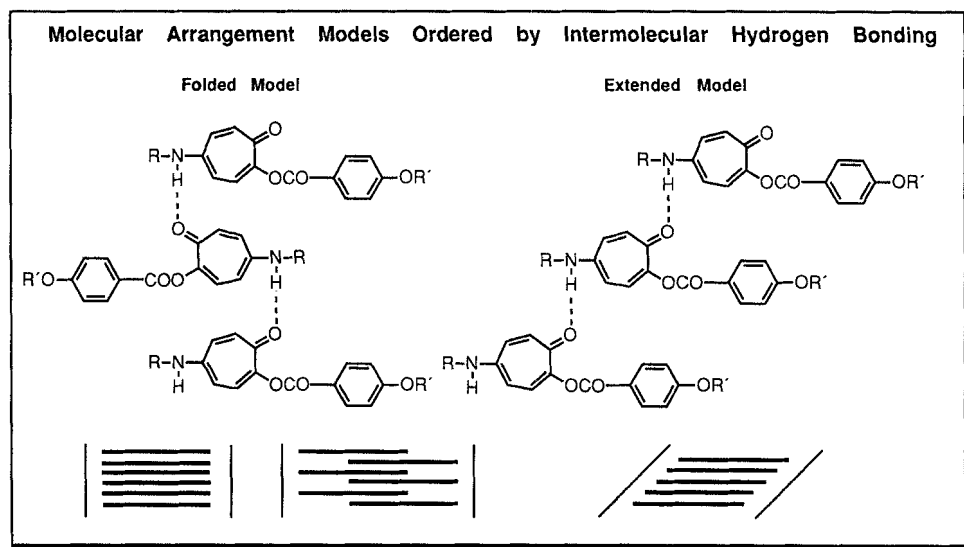


Figure 3. Molecular arrangement models for **5**.

$3287\text{ cm}^{-1}$ . The intensities of absorptions around  $1500\text{--}1550\text{ cm}^{-1}$  were increased in the liquid-crystalline state with decreasing absorption at  $1583\text{ cm}^{-1}$ . These spectral changes show that intermolecular hydrogen bonding in the liquid-crystalline state is stronger than that in the crystalline state.

On the other hand, the absorption of the ester  $\text{C}=\text{O}$  group shifted to higher wavelength in the liquid-crystalline state. This spectral change was different from those of the  $\text{NH}$  and tropone  $\text{C}=\text{O}$  groups. This implies that the interaction between the  $\text{NH}$  and ester  $\text{C}=\text{O}$  groups decreases and that between the  $\text{NH}$  and tropone  $\text{C}=\text{O}$  groups is more effective in the liquid-crystalline state. In contrast, the temperature dependent FT-IR spectra of the corresponding ether derivative (**10g**), 5-(dodecyloxy)-2-(4-dodecyloxybenzoyloxy)tropone, which exhibited the smectic C phase, did not show a marked spectral change. The temperature dependent FT-IR spectra of 2-(4-dodecylaminobenzoyloxy)-5-tetradecyloxytropone (**6d**) were measured. Raising the temperature from the crystal to the liquid-crystalline states, it showed an  $\text{NH}$  absorption around  $3320\text{ cm}^{-1}$ , a tropone  $\text{C}=\text{O}$  absorption at  $1578\text{ cm}^{-1}$ , and a sharp ester  $\text{C}=\text{O}$  absorption at  $1738\text{ cm}^{-1}$ . The spectrum of the liquid-crystalline state was almost the same as that of the crystalline state. In the isotropic liquid state, the broad  $\text{NH}$  absorption was observed around  $3377\text{ cm}^{-1}$ , and the ester  $\text{C}=\text{O}$  appeared at  $1731\text{ cm}^{-1}$  as a broad absorption band. The tropone  $\text{C}=\text{O}$  absorption at  $1578\text{ cm}^{-1}$  disappeared and coalesced with the  $\text{C}=\text{C}$  absorption at  $1609\text{ cm}^{-1}$  to give a broad band.

Lowering the temperature from the isotropic liquid state to the liquid-crystalline state, the  $\text{NH}$  and ester  $\text{C}=\text{O}$  absorptions changed slightly. The tropone  $\text{C}=\text{O}$  absorption at  $1586\text{ cm}^{-1}$  separated from the broad  $\text{C}=\text{C}$  absorption around  $105^\circ\text{C}$ , which is the transition temperature to the liquid-crystalline state. In the crystalline state, the  $\text{NH}$  absorption shifted from  $3380\text{ cm}^{-1}$  to  $3337\text{ cm}^{-1}$ , the ester  $\text{C}=\text{O}$  from  $1730\text{ cm}^{-1}$  to  $1718$  and  $1713\text{ cm}^{-1}$ , and the tropone  $\text{C}=\text{O}$  appeared at  $1584\text{ cm}^{-1}$ . These spectral changes indicated that the hydrogen bonding between the  $\text{NH}$  and the tropone  $\text{C}=\text{O}$  groups was loosened in the isotropic liquid state, but it was operative in both the crystalline and the liquid-crystalline states.

Taking the intermolecular hydrogen bonding into account, two molecular arrangement models, folded and extended, are expected for **5** as shown in figure 3. Among them, the extended model explains the appearance of the smectic C phase more favourably since the molecules are tilted with respect to the layer plane. A similar molecular model would be expected for **6**.

The IR spectra of benzenoid **11** in the crystalline state showed intermolecular hydrogen bonding between the NH and ester C=O groups. The hydrogen bonding of **11** acted not only to orientate the molecules but also to raise the melting point above the mesophase–isotropic liquid transition temperature [3]. In the case of the troponoids, since the benzoyl group migrated between the tropone C=O group and the oxygen atom at the C-1 position in the mesophase [1], the intermolecular hydrogen bonding was loosened by the [1,9] sigmatropy to avoid raising the melting point above the mesophase–isotropic liquid transition temperature.

It is known that a molecule with long terminal chains exhibits a smectic phase [10]. Compounds **5** and **6** with shorter chains are non-mesogenic since the intermolecular hydrogen bonding raises the melting point above the mesophase–isotropic liquid transition temperature. In **5** and **6** with longer chains, the intermolecular hydrogen bonding aids the appearance of the smectic C phase.

It is noteworthy that the intermolecular hydrogen bonding between the tropone carbonyl group and the NH group enhanced the appearance of the smectic C phase. Thus, the tropone carbonyl, which makes the molecular width of troponoids wider, was significant for mesogenicity to occur and for the exclusive formation of the smectic C phase.

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