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Assistance of the Intermolecular Hydrogen Bonding on the Appearance of the Smectic C Phase in 2-(4-Alkoxybenzoyloxy)-5-alkylaminotropone Liquid Crystals

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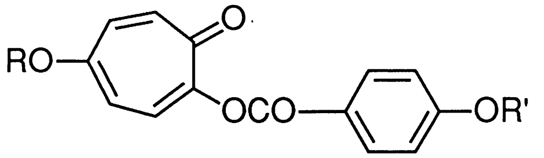
New 2-(4-alkoxybenzoyloxy)-5-alkylaminotropone liquid crystals, which exhibited the smectic C phase exclusively, were prepared. The FT-IR spectra of 2-(4-dodecyloxybenzoyloxy)-5-octadecylaminotropone at various temperatures indicated that the intermolecular hydrogen bonding between the NH and the tropone C=O groups assists the appearance of the smectic C phase.

It is known that molecular interactions play an important role on not only the appearance but also the thermal stability of the mesophase. The hydrogen bonding is one of the typical molecular interactions to order the molecules, but it has a negative factor in respect to the appearance of the mesophase since it raises the melting point above the mesophase-isotropic liquid transition temperature.1) However, the hydrogen bonding functions to exhibit the mesophase by forming stable dimers in aromatic acids2) and monosaccharides.3) Recently, Fréchet et al. reported new liquid crystalline complexes between two different components.4) Thus, the hydrogen bonding enhances the appearance of the mesophase in certain instances.

Recently, we prepared a new class of liquid crystals with 5-alkoxy-2-(4-alkoxybenzoyloxy)- (**1**)5) and 2-acyloxy-5-alkoxytropone (**2**)6) units as a core part. The latter was an example of rod-type monocyclic liquid crystals. Herein, we report the preparation of new liquid crystals from 5-aminotropolone, whose amino substituent could order the molecules through the hydrogen bonding.

2-(4-Alkoxybenzoyloxy)-5-alkylaminotropones (**3**) were prepared by the monoalkylation of 5-aminotropolone (**4**) at C-5 position and the subsequent benzoylation. 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 Table 1 together with those of **1**.5,7) When the mesophases were compared between **3** and **1**, the latter showed the nematic and the smectic C phases whereas the former did the smectic C phase exclusively. It is noteworthy that the different properties arose only by changing the heteroatom at C-5 of tropones from oxygen to nitrogen.



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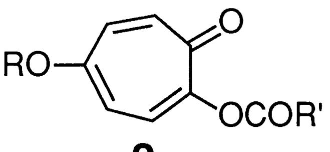

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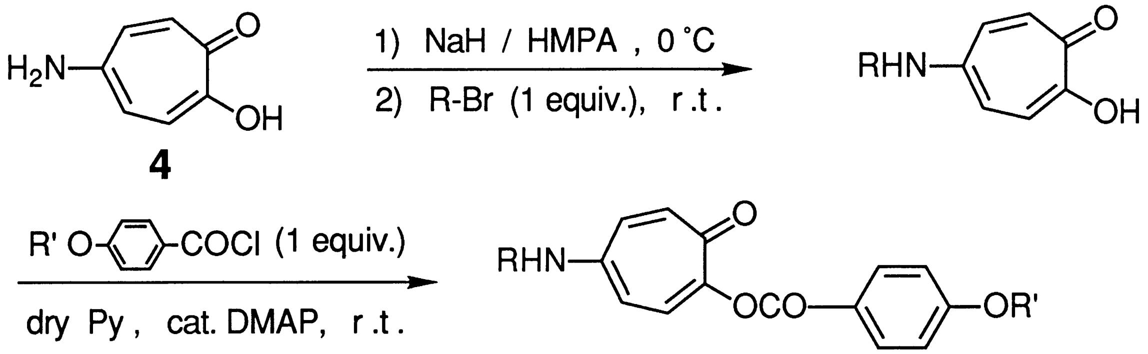

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Table 1. Transition Temperatures and Enthalpy Changes of **1** and **3**[a)]

	R	R′	**3**	**1**
			Transition temp / °C (ΔH / kJ·mol^{-1})	
a	C_6H_{13}	$C_{12}H_{25}$	K $\xrightleftharpoons[96\ (23.4)]{102\ (22.9)}$ Iso	K $\xrightarrow{58(48.3)}$ N $\xrightleftharpoons[66(2.8)]{66(1.7)}$ Iso N $\xrightarrow{54(0.7)}$ Sc $\rightarrow$ K
b	C_8H_{17}	$C_{12}H_{25}$	K $\xrightleftharpoons[90\ (24.6)]{100\ (23.0)}$ Iso	K $\xrightleftharpoons{67(34.8)}$ Sc $\xrightleftharpoons[76(5.6)]{76(4.3)}$ Iso
c	$C_{11}H_{23}$	CH_3	K $\xrightleftharpoons[120\ (43.6)]{137\ (41.5)}$ Iso	K $\xrightarrow{66(41.8)}$ Iso Iso $\xrightarrow{45(1.7)}$ N $\rightarrow$ K
d	$C_{11}H_{23}$	$C_{12}H_{25}$	K $\xrightarrow{94\ (24.4)}$ Iso Iso $\xrightarrow{91}$ Sc $\xrightarrow{88}$ K	K $\xrightleftharpoons{51(54.4)}$ Sc $\xrightleftharpoons[85(6.3)]{85(7.1)}$ Iso
e	$C_{12}H_{25}$	CH_3	K $\xrightleftharpoons[111\ (46.6)]{133\ (45.5)}$ Iso	K $\xrightarrow{71(42.3)}$ Iso Iso $\xrightarrow{50(2.1)}$ N $\xrightarrow{44(34.7)}$ K
f	$C_{12}H_{25}$	C_4H_9	K $\xrightleftharpoons[87\ (24.0)]{95\ (22.6)}$ Iso	K $\xrightarrow{64(24.3)}$ N $\xrightleftharpoons[70(5.4)]{70(4.6)}$ Iso N $\xrightarrow{63}$ Sc $\rightarrow$ K
g	$C_{12}H_{25}$	$C_{12}H_{25}$	K $\xrightarrow{96\ (25.2)}$ Iso Iso $\xrightarrow{95(8.3)}$ Sc $\xrightarrow{88(14.8)}$ K	K $\xrightleftharpoons{64(69.0)}$ Sc $\xrightleftharpoons[90(10.0)]{90(9.6)}$ Iso
h	$C_{14}H_{29}$	$C_{12}H_{25}$	K $\xrightleftharpoons[87\ (24.9)]{99\ (18.3)}$ Sc $\xrightleftharpoons[103\ (17.9)]{104\ (16.5)}$ Iso	K $\xrightleftharpoons{80\ (119.6)}$ Sc $\xrightleftharpoons[95\ (16.0)]{95\ (16.3)}$ Iso
i	$C_{18}H_{37}$	$C_{12}H_{25}$	K $\xrightleftharpoons[86\ (29.6)]{98\ (14.9)}$ Sc $\xrightleftharpoons[104\ (14.8)]{105\ (9.2)}$ Iso	K $\xrightleftharpoons{85\ (129.0)}$ Sc $\xrightleftharpoons[95\ (18.9)]{95\ (12.8)}$ Iso

a) K: Crystals, Iso: Isotropic Liquid, N: Nematic Phase, S_C: Smectic C Phase.

In Fig. 1 is shown the temperature-dependent FT-IR spectra of 5-(dodecylamino)-2-(4-dodecyloxybenzoyloxy)tropone (**3g**), which exhibited the smectic C phase monotropically. The large spectral changes were observed in the NH absorption around 3400 cm^{-1}, in the ester C=O absorption around 1700-1730 cm^{-1}, and in the tropone C=O and C=C absorptions around 1500-1600 cm^{-1}. On the other hand, the C-H stretching absorption around 2800-3000 cm^{-1} and the C=C absorption of the benzene ring around 1620 cm^{-1} changed slightly. From these observations, intermolecular hydrogen bondings between the NH group and the ester and the tropone C=O groups were predicted. The absorption of the NH stretching appeared at 3387 cm^{-1} in the crystalline state and that in the liquid crystalline state at 3287 cm^{-1}. The intensities of absorptions around 1500-1550 cm^{-1} were increased in the liquid crystalline state with decreasing the absorption at 1583 cm^{-1}. These spectral changes show that the 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 C=O group shifted to the higher wave length in the liquid crystalline state. This spectral change was different from those of the NH and tropone C=O groups. This implies that the interaction between the NH and the ester C=O groups is decreasing and that between the NH and the tropone C=O groups is more effective in the liquid crystalline state.

In contrast, the temperature-dependent FT-IR spectra of the corresponding ether derivative (**1g**), 5-(dodecyloxy)-2-(4-dodecyloxybenzoyloxy)tropone, which exhibited the smectic C phase, did not show a marked spectral change.

Taking the intermolecular hydrogen bonding into account, two molecular arrangement models, folded and extended ones, are expected as shown in Fig. 2. Among them, the extended model is more favorable to explain the appearance of the smectic C phase since molecules are tilted with respect to the layer plane.

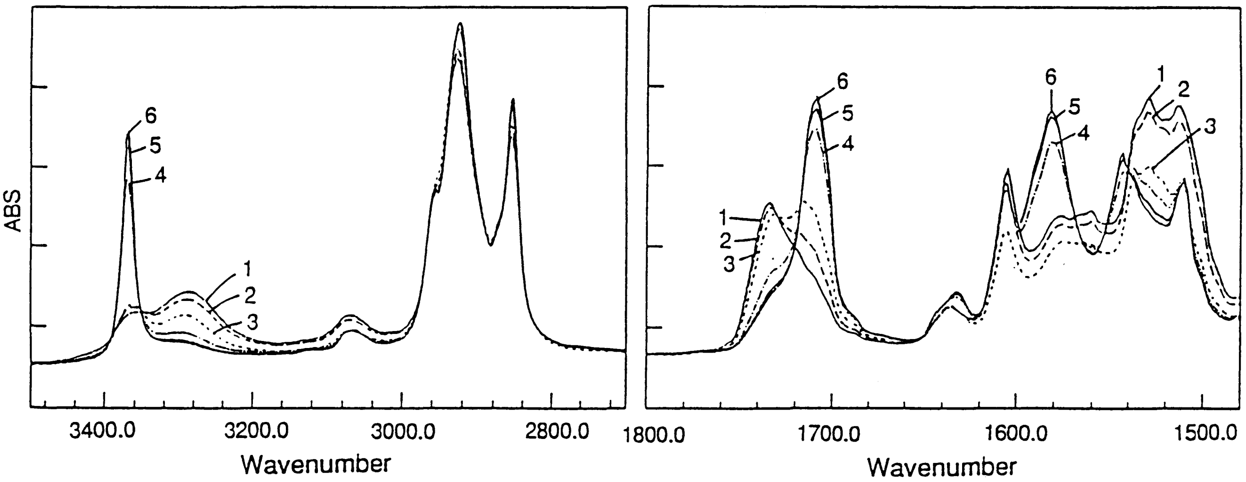

Fig.1. Variable-temperature FT-IR spectra of 5-(dodecylamino)-2-(4-dodecyloxybenzoyloxy)tropone (**3g**). Curve 1: at 100 °C, Curve 2: at 95 °C, Curve 3: at 90 °C, Curve 4: at 85 °C, Curve 5: at 80 °C, Curve 6: at 75 °C.

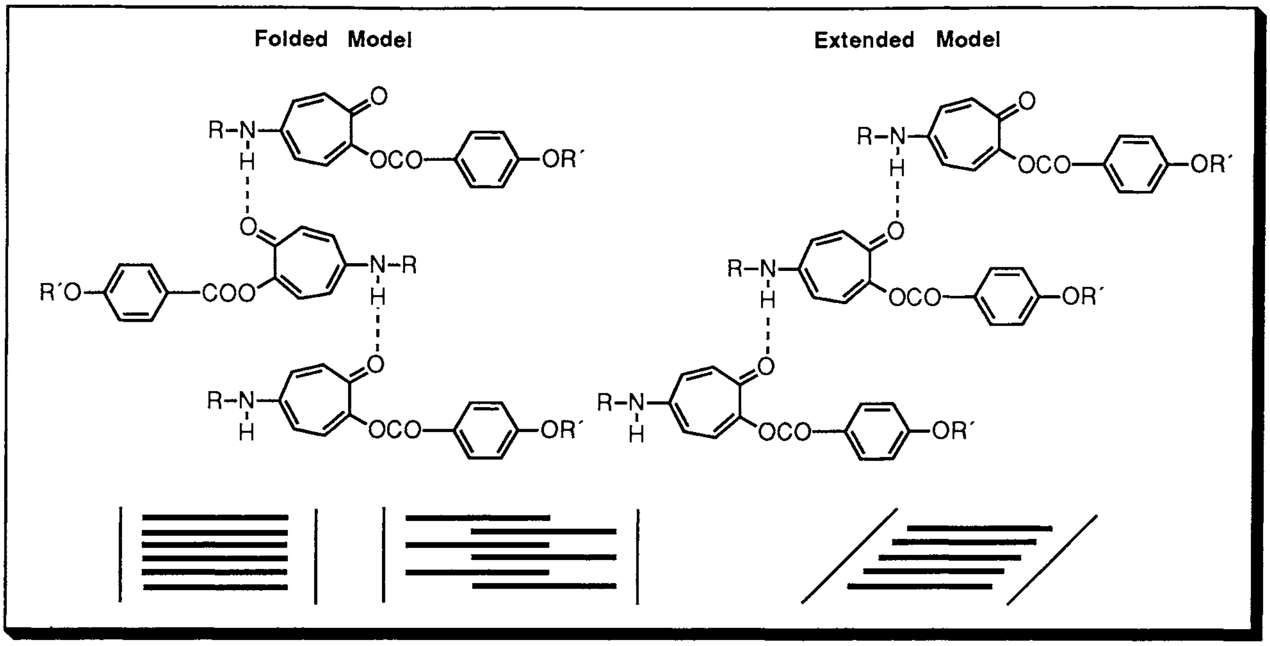

Fig. 2. Molecular arrangement models.

It is known that a molecule with long terminal chains exhibits a smectic C phase.[8] Compounds **3** with shorter chains are non-mesogenic since the intermolecular hydrogen bonding raises the melting point above the mesophase-isotropic liquid transition temperature. In **3** with longer chains, the intermolecular hydrogen bonding orders molecules to assist the appearance of the smectic C phase.

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