CHEMISTRY LETTERS, pp. 859-862, 1992.

Crucial Role of the Tropone C=O Group in Preferential Exhibition of Smectic C Phase through Intermolecular Hydrogen Bonding

Akira MORI,* Ryuko NIMURA,† 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
††Department of Organic Synthesis, Faculty of Engineering, 36, Kyushu University,
Hakozaki, Fukuoka 812

New 5-alkoxy-2-(4-alkylaminobenzoyloxy)tropones showing a smectic C phase exclusively were prepared. The corresponding benzenoids were non-mesogenic. The variable-temperature FT-IR spectra of 2-(4-dodecylaminobenzoyloxy)-5-tetradecyloxytropone suggested the intermolecular hydrogen bonding between the NH and both the tropone and the ester C=O groups in the mesophase.

The hydrogen bonding is one of the typical interactions to regulate a molecular arrangement. Even in thermotropic liquid crystals, the hydrogen bonding plays an important role to exhibit mesogenic properties as shown in the examples that aromatic acids1) and monosaccharides2) form stable dimers to show the mesophase.

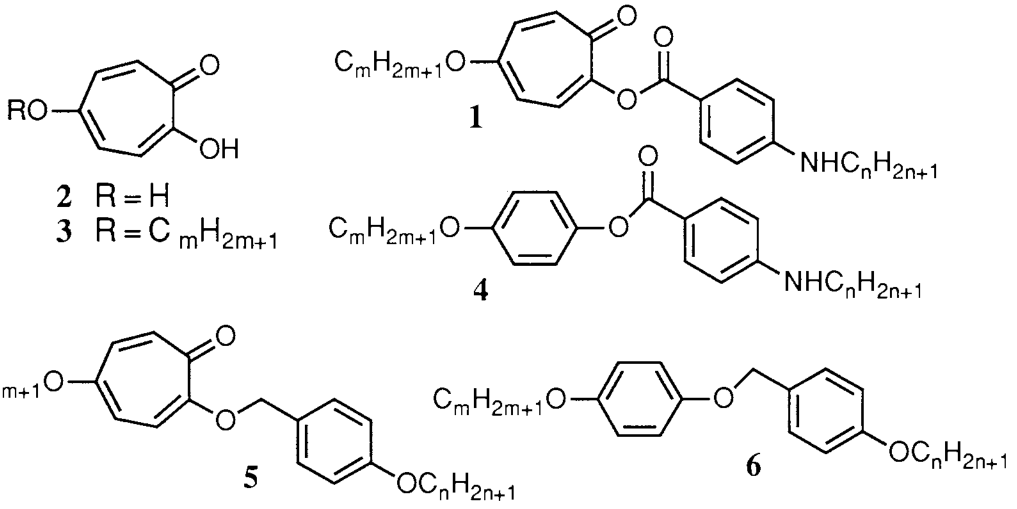
Recently, Kato et al. reported new liquid crystalline complexes through the intermolecular hydrogen bonding between two different components.3) We also reported that the intermolecular hydrogen bonding between the NH and the tropone C=O groups in the self assembly assisted the appearance of the smectic C phase.4)

In this paper, we report the crucial role of the tropone C=O group of the troponoid liquid crystals with the NH group by comparison with the corresponding benzene derivatives, which were non-mesogenic.

5-Alkoxy-2-(4-alkylaminobenzoyloxy)tropones (**1**) were prepared by means of the monoalkylation of 5-hydroxytropolone (**2**) at C-5 position and the subsequent benzoylation of 5-alkoxytropones (**3**) with 4-alkylaminobenzoyl chloride.5) The phase transition temperatures were determined using a differential scanning calorimeter (DSC) and the mesomorphic phase was observed by means of a polarizing microscope equipped with a hot stage. The results are summarized in Table 1 together with those of the corresponding benzene derivatives, 4-alkoxyphenyl 4-alkylaminobenzoates (**4**), which were prepared similarly from hydroquinone.

Compounds **1** showed a smectic C schlieren texture, whereas the corresponding **4** were non-mesogenic. The mesogenic property was dependent on the core structure, i.e., the presence of the tropone carbonyl group. It was expected that the tropone C=O group with permanent dipole moment stabilizes the smectic phase by increasing the attractive dispersion force[6] between molecules as has been observed in **5** and **6**. The former was mesogenic, but the latter was not.[7]

Additionally, compounds **1** have a [1,9] sigmatropic system, which made it to be mesogenic,[5] while the benzenoid **4** has no such a system.



1

2 R = H
3 R = C_mH_{2m+1}

4

5

6

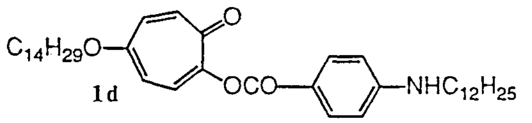
Table 1. Transition Temperatures and Enthalpy Changes of **1** and **4**[a)]

	m	n	Transition temp / °C (ΔH/kJ·mol^{-1}) 1	4
a	12	8	$\mathrm{K} \xrightarrow{108(27)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[84]{} \mathrm{Sc} \xleftarrow[90]{} \mathrm{Iso}$	$\mathrm{K} \xrightarrow{124(55)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[120(54)]{} \mathrm{Iso}$
b	12	10	$\mathrm{K} \xrightarrow{112(51)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[90]{} \mathrm{Sc} \xleftarrow[98]{} \mathrm{Iso}$	$\mathrm{K} \xrightarrow{115(33)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[108(30)]{} \mathrm{Iso}$
c	12	12	$\mathrm{K} \xrightarrow{108(50)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[101]{} \mathrm{Sc} \xleftarrow[108]{} \mathrm{Iso}$	$\mathrm{K} \xrightarrow{116(48)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[110(45)]{} \mathrm{Iso}$
d	14	12	$\mathrm{K} \xrightarrow{109} \mathrm{Sc} \xrightarrow{115} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[91(37)]{} \mathrm{Sc} \xleftarrow[106(9)]{} \mathrm{Iso}$	$\mathrm{K} \xrightarrow{115(60)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[109(52)]{} \mathrm{Iso}$
e	18	12	$\mathrm{K} \xrightarrow{108} \mathrm{Sc} \xrightarrow{111} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[95(38)]{} \mathrm{Sc} \xleftarrow[111(11)]{} \mathrm{Iso}$	$\mathrm{K} \xrightarrow{115(70)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[109(72)]{} \mathrm{Iso}$
f	18	18	$\mathrm{K} \xrightarrow{111(130)} \mathrm{Iso}$ $\mathrm{K} \xleftarrow[93]{} \mathrm{Sc} \xleftarrow[111]{} \mathrm{Iso}$	$\mathrm{K_1} \xrightarrow{106(12)} \mathrm{K_2} \xrightarrow{113(51)} \mathrm{Iso}$ $\mathrm{K_1} \xleftarrow[98(16)]{} \mathrm{K_2} \xleftarrow[106(72)]{} \mathrm{Iso}$

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

In order to specify the role of the tropone C=O group on the appearance of the mesophase, the temperature-dependent FT-IR spectra of 2-(4-dodecylaminobenzoyloxy)-5-tetradecyloxytropone (**1d**) were measured. Raising the temperature from the crystal to the liquid crystalline states, the sharp NH absorption was observed around 3320 cm^{-1}, the tropone C=O absorbed at 1578 cm^{-1}, and the sharp ester C=O at 1738 cm^{-1}. The spectrum of the liquid crystalline state was almost the same to that of the crystalline state. In the isotropic liquid state, the broad NH absorption was observed around 3377 cm^{-1}, and the ester C=O appeared at 1731 cm^{-1} as a broad absorption band. The tropone C=O absorption at 1578 cm^{-1} disappeared and coalesced with the C=C absorption at 1609 cm^{-1} to give the broad band.

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



1d

$$K \underset{91(36.7)}{\overset{109}{\rightleftharpoons}} S_C \underset{106(8.5)}{\overset{115}{\rightleftharpoons}} Iso$$

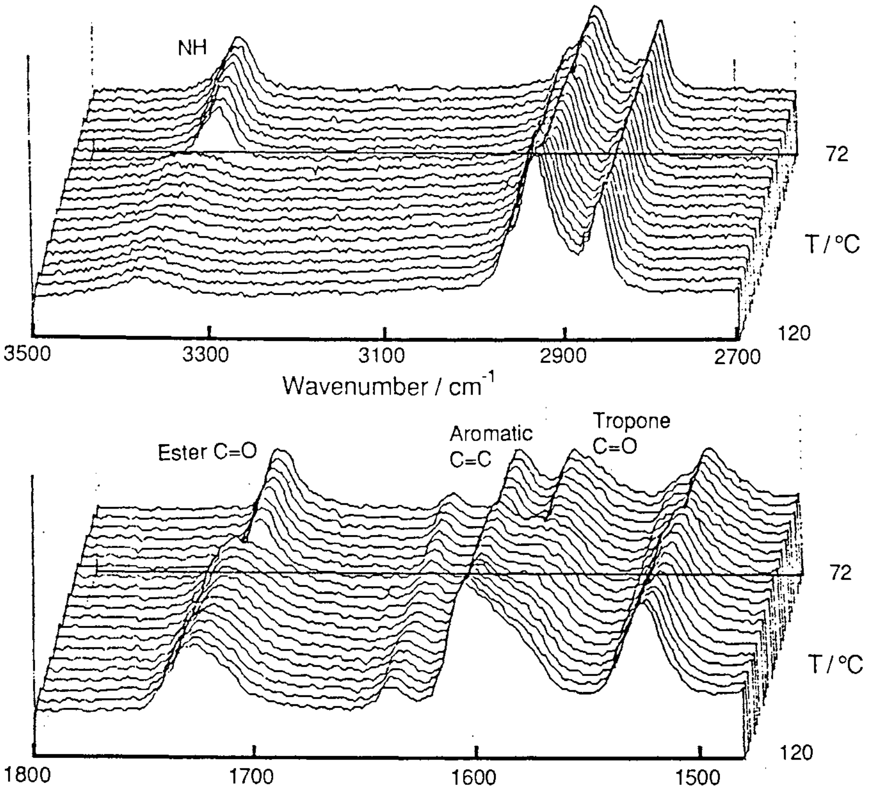


Fig.1. Variable-temperature FT-IR spectra of **1d**.

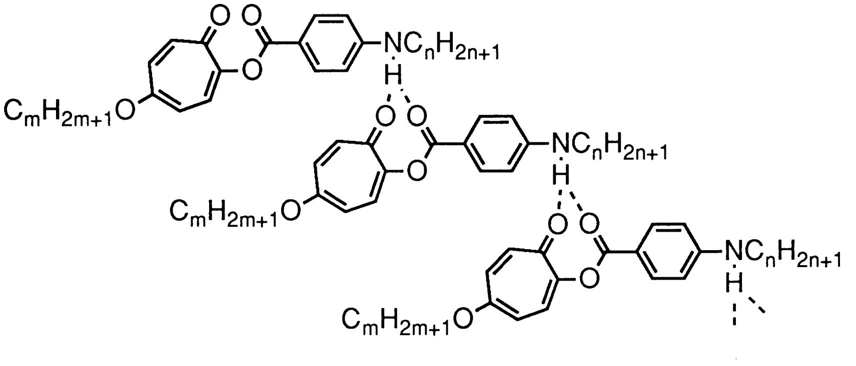


Fig. 2. Molecular arrangement model.

The IR spectra of benzenoid **4** in the crystalline state showed the intermolecular hydrogen bonding between the NH and the ester C=O groups. The hydrogen bonding of **4** acted not only to orientate the molecules but to raise the melting point above the mesophase-isotropic liquid transition temperature.8) In the case of the troponoids, since the benzoyl group migrated between the tropone C=O group and the oxygen atom at C-1 in the mesophase,5) the intermolecular hydrogen bonding was loosened by the [1,9] sigmatropy to avoid raising the melting point above the mesophase-isotropic liquid transition temperature.

In Fig. 2 is shown the molecular arrangement model, considering the intermolecular hydrogen bonding between the NH and the tropone C=O groups in the liquid crystalline state. The X-ray diffraction measurement of **1d** is now in progress.

We are grateful to Ms. Chihiro Jin (Nihon Bunko Co. Ltd.) for the measurement of the temperature-dependent FT-IR spectra. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas No. 01648519 (H. T.) and Grant-in-Aid for Scientific Research No. 02453025 (A. M.) from the Ministry of Education, Science and Culture, Japanese Government, to which our thanks are due.

References

1) G. W. Gray and B. Jones, *J. Chem. Soc.*, **1953**, 4179; R. F. Bryan, P. Hartley, R. W. Miller, and M.-S. Shen, *Mol. Cryst. Liq. Cryst.*, **62**, 281 (1980).
2) J. A. Jeffrey, *Acc. Chem. Res.*, **19**, 168 (1986).
3) T. Kato and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **111**, 8533 (1989); T. Kato, A. Fujishima, and J. M. J. Fréchet, *Chem. Lett.*, **1990**, 919; T. Kato, P. G. Wilson, A. Fujishima and J. M. J. Fréchet, *ibid.*, **1990**, 2003
4) A. Mori, R. Nimura, and H. Takeshita, *Chem. Lett.*, **1991**, 77.
5) A. Mori, M. Uchida, and H. Takeshita, *Chem. Lett.*, **1989**, 591; A. Mori, H. Takeshita, K. Kida, and M. Uchida, *J. Am. Chem. Soc.*, **112**, 8635 (1990); K. Kida, A. Mori, and H. Takeshita, *Mol. Cryst. Liq. Cryst.*, **199**, 387 (1991).
6) K. Takatoh, K. Sunohara, and M. Sakamoto, *Mol. Cryst. Liq. Cryst.*, **164**, 167 (1988).
7) A. Mori, H. Taya, and H. Takeshita, *Chem. Lett.*, **1991**, 579.
8) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, N. Y. (1962), p. 162.

(Received March 4, 1992)