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Preferential Exhibition of Smectic A Phase through Intramolecular Hydrogen Bonding in 2-Amino-5-phenyltropone Liquid Crystals

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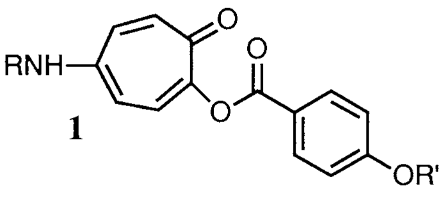
Two new types of liquid crystals, 5-(4-alkanoylaminophenyl)-2-alkanoylaminotropones and 5-(4-alkanoylaminophenyl)-2-alkanoyloxytropones, were prepared. The former showed the smectic A phase and the latter did the smectic A and C phases. The ^{1}H NMR spectra indicated the former to be in intramolecularly hydrogen-bonded *L*-shaped alignment.

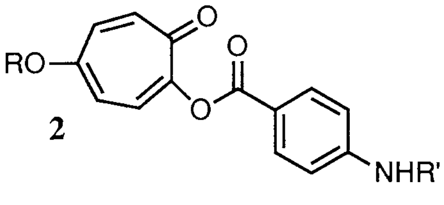
Recently, we have reported the synthesis of new liquid crystals with a 5-aminotropolone core, 2-(4-alkoxybenzoyloxy)-5-alkylaminotropones (**1**)[1] and 5-alkoxy-2-(4-alkylaminobenzoyloxy)tropones (**2**),[2] which showed a smectic C phase. The corresponding benzenoids of the latter were non-mesogenic. The variable-temperature IR spectra of **1** and **2** indicated the intermolecular hydrogen bonding between the NH and tropone carbonyl groups, which assisted the exclusive exhibition of the smectic C phase.

On the other hand, the intramolecular hydrogen bonding also assisted some systems to be mesogenic as has been observed in 3,4,5-trialkoxybenzaldehyde-2',4'-dinitrophenylhydrazone,[3] substituted Schiff's bases,[4] azo compounds,[5] and 3,4,4''-trisubstituted terphenyls.[6]

In this paper, we report the synthesis of two new types of liquid crystals, 5-(4-alkanoylaminophenyl)-2-alkanoylaminotropones (**3**) and 5-(4-alkanoylaminophenyl)-2-alkanoyloxytropones (**4**) and their thermotropic properties.



1



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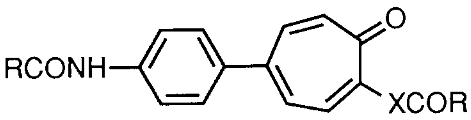
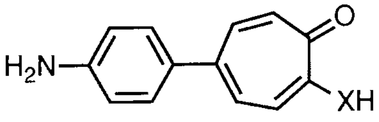


3 X = NH **4** X = O



5 X = NH **6** X = O

Compounds **3** and **4** were prepared by acylation of 5-(4-aminophenyl)-2-aminotropone (**5**) and 5-(4-aminophenyl)tropolone (**6**).[7] The phase transition temperatures were determined using a differential scanning calorimeter (DSC), and the mesomorphic phases were observed by a polarizing microscope equipped with a hot stage. The results are summarized in Tables 1 and 2. Compounds **3** showed the smectic A phase, whereas compounds **4** the smectic A phase, and the smectic C phase appeared in **4** with longer alkyl chains. Compounds **3** showed lower isotropic transition temperatures and somewhat higher melting points than compounds **4**.

Table 1. Transition temperatures and enthalpy changes for **3**[a)]

	R	Transition temp / ° C (ΔH/ kJ·mol^{-1})
a	$C_{11}H_{23}$	$\mathrm{K}\xrightleftharpoons[132\ (6.5)]{133\ (6.4)}\mathrm{K_1}\xrightleftharpoons[141\ (37.2)]{150\ (36.1)}\mathrm{S_A}\xrightleftharpoons[155\ (8.0)]{157\ (7.3)}\mathrm{Iso}$
b	$C_{13}H_{27}$	$\mathrm{K}\xrightleftharpoons[140\ (36.3)]{148\ (37.2)}\mathrm{S_A}\xrightleftharpoons[155\ (8.3)]{155\ (6.3)}\mathrm{Iso}$
c	$C_{15}H_{31}$	$\mathrm{K}\xrightarrow{130\ (1.4)}\mathrm{K_1}\xrightarrow{142\ (41.5)}\mathrm{S_A}\xrightleftharpoons[153\ (7.1)]{154\ (7.0)}\mathrm{Iso}$; $\mathrm{K}\xleftarrow[133\ (38.9)]{}\mathrm{S_A}$

a) K: Crystals, Iso: Isotropic Liquid, S_A and S_C: Smectic A and C Phases.

Table 2. Transition temperatures and enthalpy changes for **4**[a)]

	R	Transition temp / ° C (ΔH/ kJ·mol^{-1})
a	$C_{11}H_{23}$	$\mathrm{K}\xrightarrow{98\ (19.6)}\mathrm{K_1}\xrightarrow{148}\mathrm{S_C}\xrightleftharpoons{159}\mathrm{S_A}\xrightleftharpoons[175\ (8.5)]{178\ (8.4)}\mathrm{Iso}$; $\mathrm{K}\xleftarrow[134]{}\mathrm{S_C}$
b	$C_{13}H_{27}$	$\mathrm{K}\xrightleftharpoons[129\ (35.4)]{140\ (38.0)}\mathrm{S_C}\xrightleftharpoons[145]{155\ (0.3)}\mathrm{S_A}\xrightleftharpoons[164\ (9.9)]{169\ (10.9)}\mathrm{Iso}$
c	$C_{15}H_{31}$	$\mathrm{K}\xrightleftharpoons[132\ (38.1)]{137\ (44.9)}\mathrm{S_C}\xrightleftharpoons{152}\mathrm{S_A}\xrightleftharpoons[162\ (6.6)]{175\ (9.6)}\mathrm{Iso}$

a) K: Crystals, Iso: Isotropic Liquid, S_A and S_C: Smectic A and C Phases.

The mesomorphic properties of **3** and **4** are due to the difference of the heteroatom at C-2 of the tropone nucleus. The ^1H NMR spectra of **4** showed a [1,9] sigmatropy[8] in $CDCl_3$, while those of **3** did not. The ^1H NMR spectra of **3** displayed an olefinic proton around δ 9.1 as a doublet (*J*=11 Hz), which was assigned to H-3. This low field shift was caused by the anisotropy of the adjacent amide C=O group, which is located at the outer side of the molecule because of the intramolecular hydrogen bonding between the tropone C=O and the NH groups. The two singlet signals due to the NH of **3b** appeared at δ 7.29 and 9.37. The latter signal was assigned to the intramolecularly hydrogen-bonded NH proton. In the D_2O exchanging experiment of **3b**, these two NH protons disappeared and the doublet at δ 9.06 (*J*=10.6 Hz) remained unchanged.

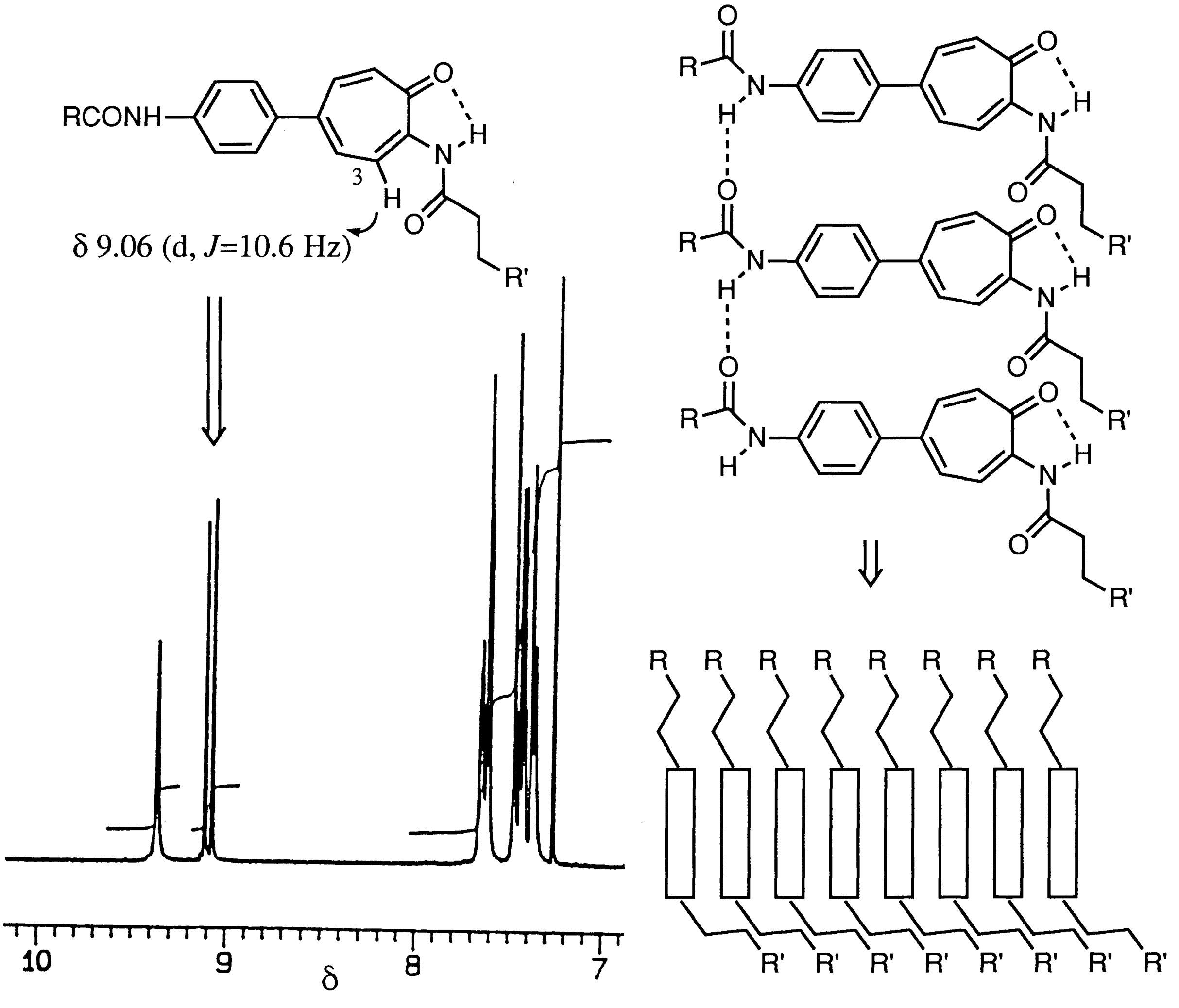


Fig. 1. ^1H NMR Spectrum ($CDCl_3$, 270 MHz) of **3b** and molecular packing model for **3**.

Previously, we postulated a molecular arrangement model to explain the exclusive exhibition of the smectic C phase for **1** and **2**, considering the intermolecular hydrogen bonding.[1,2] Since **4** has the similar chromophore to **1**, it is possible for **4** to make an intermolecular hydrogen bonding. However, since **4** with shorter alkyl chains showed the smectic A phase, and **4** with longer alkyl chains the smectic C phase, the situation of **4** was not the same as those of **1** and **2**. Dissimilarity is explained in terms of the effect of the alkyl chain length on the appearance of a smectic phase; the longer alkyl chain promoted the appearance of a smectic C phase.[9]

It is evident from ^1H NMR spectrum of **3** that the NH and tropone C=O groups made an intramolecular hydrogen bonding in $CDCl_3$ solution. Even in the liquid crystalline states, it is speculated that the intramolecular hydrogen bonding is operative to form an *L*-shape species.[10] The *L*-shape molecules are likely to be packed as shown in Figure 1 to reduce the molecular volume. The intermolecular hydrogen bonding between the amide groups on the phenyl group would assist the arrangement of molecules. This molecular arrangement would induce the smectic A phase.[11] The intramolecular hydrogen bonding can reduce the molecular motion to give the rigidity, whereas the [1,9] sigmatropic system can keep the rod-shape of the molecule. The heteroatom on the seven-membered ring thus controlled the molecular structure to affect the liquid property.

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