higher coordination numbers of the lanthanide metal ions may be also responsible for the increased capacity factors denoted by k_1' or k_2' in Table 1 as compared to those with Cu^{2+}.[6,7]

It is well known that ligand field stabilization energies are very small for the lanthanide metal ions and the thermodynamic properties of the lanthanide complexes can be fairly accurately correlated by the electrostatic consequences of charge and size.[8] If the interaction between lanthanide metal ion and resolving α-amino acid is mainly electrostatic, one can expect the steady increase in the capacity factors as the atomic number of lanthanide increases. However, the variation in the capacity factors according to the lanthanide metal ions does not show any notable trend. This may stem from the fact that the considerable change in size of the lanthanide ions from La^{3+} (1.17 Å) to Ho^{3+} (1.04 Å) might result in appreciably different structure among homologous lanthanide complexes with α-amino acids as suggested by other workers.[9]

In conclusion, we elucidated that lanthanide metal ions can be used to form energeticaly different two diastereomeric complexes with the fixed chiral ligand (chiral selector) and the two enantiomers of mobile recemic α-amino acid for the resolution of α-amino acids without derivatization in chiral ligand exchange chromatography. The use of lanthanide metal ion instead of Cu^{2+} ion was found to increase the capacity factors. However, any trend in the capacity factors according to the lanthanide metal ions was not observed. The higher nuclear charge, higher coordination numbers of lanthanide metal ions and the variation in the structure of homologous lanthanide complexes originated from appreciably different radii of lanthanide ions were presumed to be responsible for the increased capacity factors without any notable trend.

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Comparison of Liquid Crystalline Behavior of *N*-(4-n-Alkyloxybenzylidene)-4'-n-butylanilines and *N*-(4-n-Alkyloxybenzylidene)-4'-*p*-aminocinnamates

Jung-Il Jin and Jin-Wook Shin

Department of Chemistry, Korea University,
1-Anam Dong, Seoul 136-701

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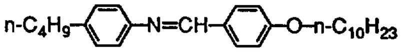
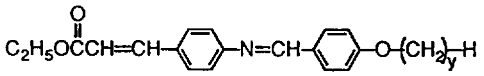
There have been much efforts to establish structure-property relationship of low molar mass thermotropic compounds.[1-4] While we have been conducting an investigation on the mesomorphic properties of dimesogenic and multimesogenic compounds,[5-8] we have found that the following three compounds have not been yet reported. Therefore, we became interested in their synthesis and comparing the liquid crystalline properties thereof.



I-10



II-5 (y=5) , II-10 (y=10)

N-(4-n-Pentyloxybenzylidene)-4'-n-butylaniline(**I-5**) was reported earlier by Smith and coworkers.[9]

Results and Discussion

Thermal transition behavior of compounds **I-5**(*N*-(4-n-pentyloxybenzylidene)-4'-n-buthylaniline), **I-10**, **II-5** and **II-10** are summarized in Table 1 together with the nature of mesophases they reveal. The data for **I-5** are quoted from reference 9. Identification of the mesophases formed by these compounds was performed by the examination of their optical textures observed through a cross-polarized microscope equipped with a hot-stage.[10,11] The DSC thermograms of **II-5** and **II-10** are shown in Figure 1. The thermograms were obtained at the heating and cooling rates of 10℃/min. All of the present compounds are enantiotropically thermotropic and did not form any additional monotropic phase on cooling, see Figure 1. One interesting observation made on the crystallization behavior of the compounds is that the compound

Table 1. Phase Transition and Liquid Crystalline Phases*

Compound	T_1	T_2	T_3	T_4
I-5	12($K \rightarrow S_B$)	52.1($S_B \rightarrow S_A$)	52.4($S_A \rightarrow N$)	69.0($N \rightarrow I$)
I-10	48($K \rightarrow S_B$)	70.3($S_B \rightarrow S_C$)	73 ($S_C \rightarrow S_A$)	85.8($S_A \rightarrow I$)
II-5	66($K \rightarrow S_C$)	131 ($S_C \rightarrow S_A$)	162 ($S_A \rightarrow N$)	
II-10	68($K \rightarrow S_C$)	116 ($S_C \rightarrow S_A$)	155 ($S_A \rightarrow N$)	

*K and I stand for crystalline solid and isotropic phase, respectively. The data for compound **I-5** were taken from ref. 9.

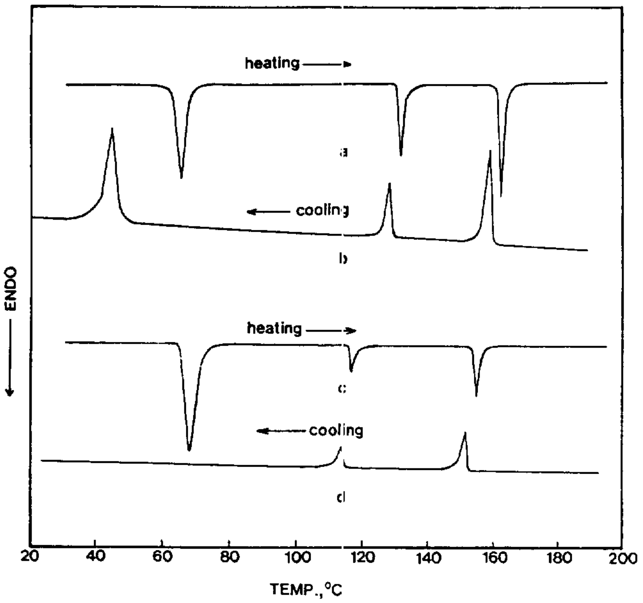


Figure 1. DSC thermograms of compounds **II-5** and **II-10**; a and c are for heating and b and d for cooling. Both heating and cooling rates were 10℃/min.

II-10 is very slow in crystallization and does not show crystallization exotherm on the cooling DSC curve down to room temperature (Figure 1d). Others crystallized on cooling the liquid crystalline phases, although supercooling was significant as shown by Figure 1b.

Discussing about the liquid crystalline behavior of the present compounds, **I-5**[9] was reported to melt at 12℃ to liquid crystalline S_B(smectic B) phase followed by transitions to S_A (smectic A) and N(nematic) phases at 52.1℃ and 52.4℃, respectively. And then it finally undergoes isotropization at 69 ℃. **II-10** carries a longer decyloxy terminal alkoxy group and shows much different phase transitions when compared with **I-5** with the shorter n-petyloxy terminal group. First of all, **I-10** melts at a higher temperature(48℃) into S_B phase. The higher melting temperature can be ascribed to a stronger lattice force in the solid crystal due to an effective packing assisted by the longer linear alkoxy substituent. This compound goes through S_C and S_A phases before isotropization. This compound does not form a nematic phase as **I-5** does. It has been very well documented for a wide variety of thermotropic compounds[12] showing that increasing the length of a terminally located n-alkyl group favors smectic mesophase-formation. And this compound is of no exception.

As one can see from Table 1, compounds **II-5** and **II-10**

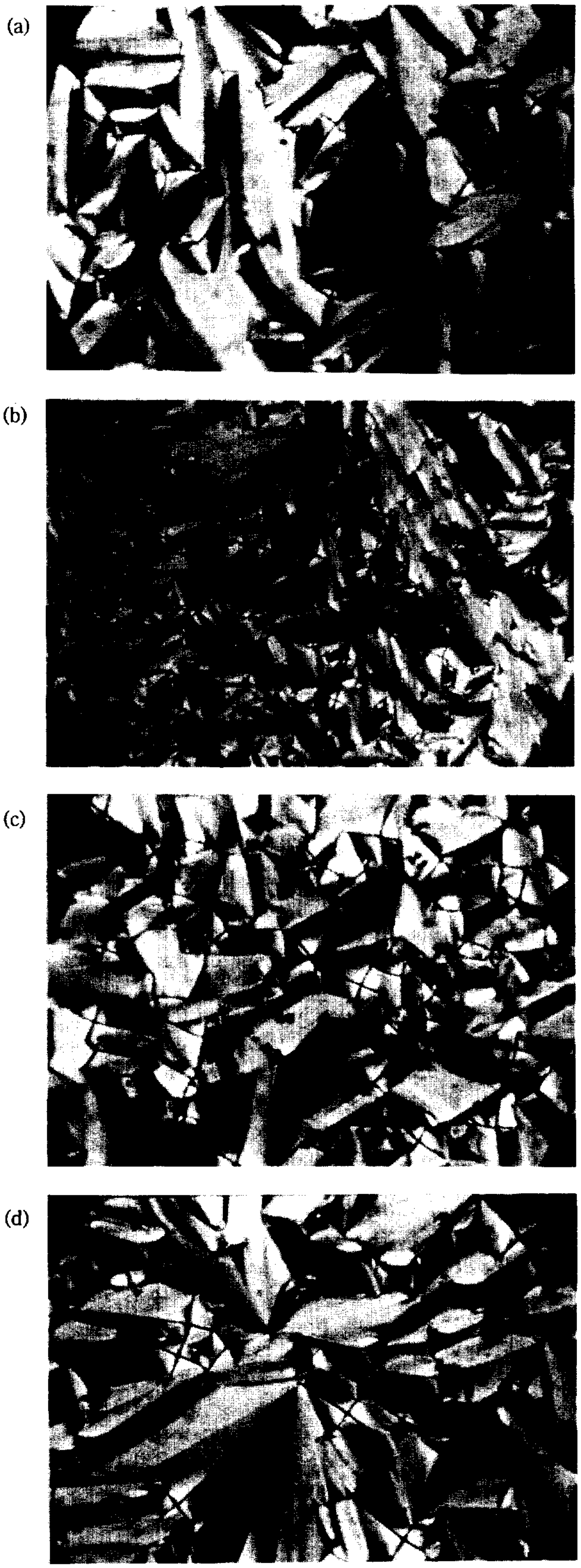


Figure 2. Photomicrographs of (a) **II-5** at 131℃, (b) **II-5** at 159 ℃, (c) **II-10** at 106℃, and (d) **II-10** at 153℃ (Magnification 200 ×). All photographs are taken on cooling isotropic melts.

melt at much higher temperatures than the corresponding I-compounds. The presence of much longer rigid core part in these compounds must be the major reason. One peculiar phenomenon noted for compound **II-5** is the fact that the relative area of the crystal→S_C transition endothermic peak to those of the other transition peaks is significantly smaller when compared with the corresponding area of **II-10**. The area of melting endotherm of **II-5** is only 45% of the total areas of the three endothermic peaks, whereas the value for **II-10** is 72%. Although the reason is not yet clear, one reasonable conjecture is that somehow the lattice energy of **II-5** is lower when compared with that of **II-10**. There are many reports that show relatively lower heat of melting for the other types of compounds[13,14] containing the odd numbered pentyl or pentyloxy terminal group.

Both **II-5** and **II-10** melt into S_C phase and go through S_A phase before isotropization. Figure 2a-d show their optical textures observed through a polarizing microscope. Figure 2a and 2c are of the typical broken fan texture characteristic to a S_C phase and Figure 2b and 2d are of the fan texture typical to a S_A phase. As mentioned above, **I-5** forms a nematic phase, whereas **II-5** does not. This implies that the compounds of type II more favor the formation of smectic phases. This difference can be explained by their structural differences: 1) the compounds II contain a longer rigid core and 2) the lateral intermolecular interaction is expected to be stronger for II-compounds than I-compounds due to a larger lateral permanent dipole moment arising from the presence of the polar, bent ester group. These two factors both will enhance the stability of the smectic phases.[15] We, indeed, observe that isotropization temperatures of **II-5** (162℃) and **II-10** (155℃) are extremely higher than those of **I-5** (69℃) and **I-10** (85.8℃).

In conclusion, alkoxybenzylidene aminocinnamates seem to favor the formation of the smectic phases when compared with alkoxybenzylidene anilines, and the formers' isotropization temperatures are much higher than those of the latters. This differences arise mainly from the goemetric factor of the rigid core part and the overall electronic structure of the molecules.

Experimental

Synthesis of Compound I-10. 4-n-Butylaniline (2.98 g; 2.0×10^{-2} mole) and 4-decyloxybenzaldehyde (5.24 g; 2.0×10^{-2} mole) were dissolved in 40 *ml* of ethanol and the mixture was refluxed for 3 hours. The mixture was then poured into large excess distilled water. The precipitate was collected and recrystallized from petroleum ether. The product yield was 85%, mp. 48℃. ^{1}H-NMR ($CDCl_3$): δ 8.2 (s, 1H, CH=N-), 6.8-7.8 (m, 8H, aromatic), 3.9 (t, 2H, C_6H_5-O-$\underline{CH}_2$-), 2.6 (t, 2H, C_6H_5-$\underline{CH}_2$), 0.8-2.0 ppm (m, 26H, aliphatic). IR ($CHCl_3$): 2950 (alphatic C-H stretching), 1720 (C=O stretching), 1640 (C=N-stretching), 1610 (aromatic C=C stretching). Anal.: Calcd. C 82.37, H 10.01, N 3.56%; Found C 82.29, H 10.10, N 3.49%.

Synthesis of Compound II-5. Ethyl 4-aminocinnamate (2.01 g; 1.05×10^{-2} mole) and 4-pentyloxybenzaldehyde (2.02 g; 1.05×10^{-2} mole) were dissolved in 50 *ml* of ethanol. The mixture was refluxed for 4 hours and cooled to 0℃. The precipitate was collected and recrystallized from ethanol. The yield was 3.31 g (86.3%), mp. 66℃. ^{1}H-NMR ($CDCl_3$): δ 8.3 (s, 1H, CH=N-), 6.3-7.9 (m, 10H, aromatic and -CH=CH-), 4.3 (q, 2H, $-CH_2O\overset{\overset{O}{\|}}{C}-$), 3.9 (t, 2H, $C_6H_5O\underline{CH}_2$), 0.7-2.0 ppm (m, 14H, aliphatic). IR ($CHCl_3$): 2950 (C-H stretching), 1720 (C=O stretching), 1640 (C=N-stretching), 1610 (aromatic C=C stretching), 980 cm^{-1} (*trans*-vinylene =C-H out-of-plane bending).

Anal.: Calcd. C 75.57, H 7.46, N 3.83%; Found C 75.49, H 7.53, N 3.79%.

Compound **II-10** was synthesized by the similar way and the product yield was 86%, mp. 68℃. The IR- and ^{1}H-NMR spectra agree with those expected. Anal.: Calcd. C 77.19, H 8.58, N 3.22%; Found C 77.12, H 8.66, N 3.17%.

Thermal Analysis and Microscopy. The DSC thermograms of the compounds were obtained on a DuPont 910 Thermal Analyzer under N_2 atmosphere with a heating or cooling rate of 10℃/min. Indium was utilized as a reference for temperature calibration. The optical textures and thermal transitions were observed on a polarizing microscope (Leitz, Ortholux) equipped with a hot stage (Mettler FP-2). Magnification was 200.

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