Synthesis of New Homologous Series of Schiff Base Liquid Crystals with Iodo Terminal Group

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Abstract
A series of Schiff base ester, 4-{[(4-iodophenyl)imino]methyl}phenyl alkanoates possessing different number of carbon atoms at the terminal alkanoyloxy chain ($C_{n-1}H_{2n-1}COO$-, n = 4, 6, 8, 10, 12, 14) was synthesized. C4 member was found non-mesogenic, whilst C6 to C14 derivatives exhibited enantiotropic smectic A phase with fan-shaped texture. It was found that the length of terminal alkanoyloxy chain influenced the mesomorphic properties.

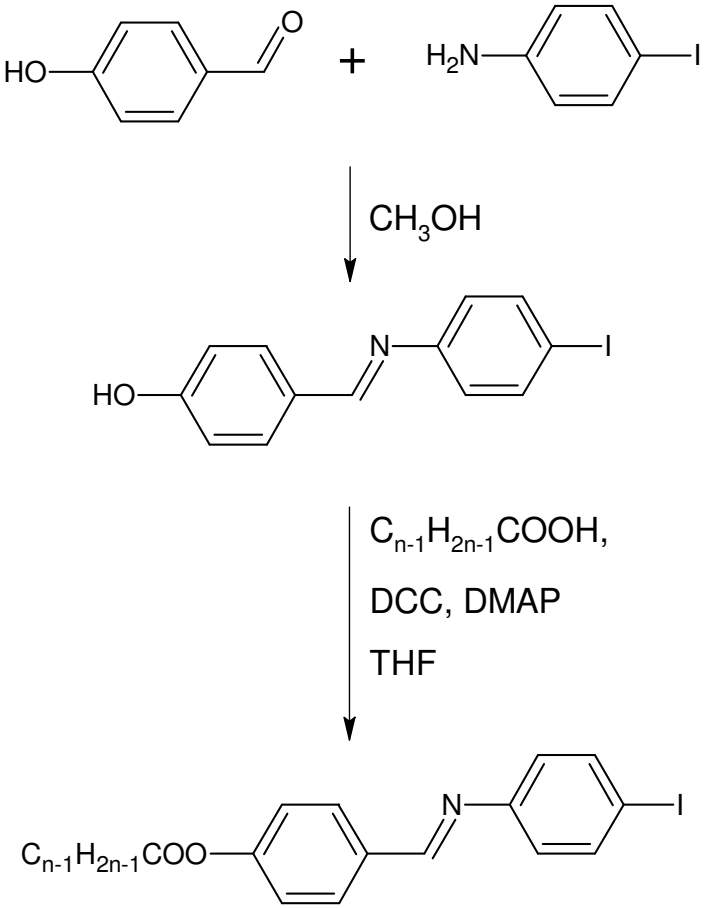
Keywords: Schiff base, mesomorphic, smectic, enantiotropic

Introduction
Understanding of structure–property relationship is fundamental of molecular modifications for synthesis of new mesogens with desirable properties and applications [1]. An earlier report has shown that low-mass molecules containing two unsaturated rings with one or multiple terminal substituents are capable of exhibiting mesomorphic properties [2]. Discovery of 4-methoxybenzylidene-4′-butylaniline and its application of nematic phase at room temperature in displays sparked a renewed interest of researcher on establishing structure–property relationships of Schiff base esters [3,4].

In our previous studies, the results revealed that Schiff base and ester are useful linking units for generating mesomorphism in thermotropic liquid crystals with two and three aromatic rings. Aromatic azomethine ester comprising of different polarity of substituents has been known to either promote or suppress the mesomorphic properties [5-8]. In order to accomplish the research on mesomorphic properties of two aromatic rings Schiff base ester, we reported another homologous series of Schiff base esters, 4-{[(4-iodophenyl)imino]methyl}phenyl alkanoates.

Synthesis
4-Iodoaniline was condensed with 4-hydroxybenzaldehyde upon refluxing in methanol for an hour. Then, the intermediate compound (Schiff base) was esterified with fatty acids in the presence of N,N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). All the crude products were recrystallized using ethanol until constant melting points were obtained.

Synthetic Scheme



where n = 4, 6, 8, 10, 12, 14

Results and Discussion

The liquid crystalline textures of the title compounds were observed under polarizing optical microscope (POM) and phase identification was made by comparing the observed textures with those reported in the literature [9,10].

All the compounds exhibited enantiotropic smectic A (SmA) phase with fan-shaped texture except *n*-butanoyloxy derivative. Optical photomicrograph of C4 derivative displaying SmA phase is depicted in the Figure 1 as the representative for all the members in the series.

A plot of phase transition temperatures against number of carbon atoms (n) in alkanoyloxy chain during heating scan is shown in Fig. 2. Based on the plot, it can be deduced that length of terminal alkanoyloxy chain influenced the mesomorphic properties. With the increasing length of terminal chain, the phase changed from non-mesogenic (C4 derivative) to enantiotropic smectic A phase (C6-C14 derivatives). Smectic A phase range increased from C6 to C10 derivatives. This is because the increase of length of terminal alkanoylxy chain led to the enhancement of the smectic properties. However, smectic A phase range for C12 and C14 derivatives showing descending trend due to the dilution of mesogenic core [11,12].

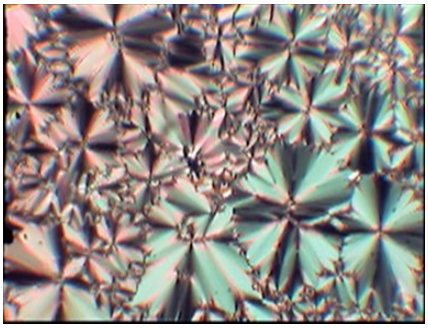


Fig. 1. Optical photomicrograph of C4 derivative exhibiting fan-shaped texture of smectic A phase during cooling cycle.

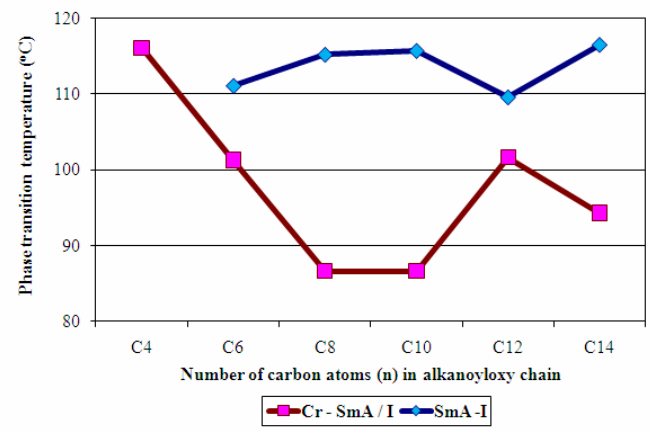


Fig. 2. Plot of phase transition temperatures against number of carbon atoms (n) in alkanoyloxy chain.

Conclusion

All the synthesized compounds are enantiotropic SmA liquid crystals except for C4 derivative which having the shortest alkanoyloxy chain.

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