Synthesis and Properties of Non-chiral Liquid Crystalline Molecules with Semi-Fluorinated Alkyl Chains

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Abstract

In this paper, new non-chiral molecules with semi-fluorinated alkyl chains were synthesized varying the structure of central bent core unit. Their mesomorphic properties were investigated by DSC and polarized microscopy. The compound with 1,3-dihydroxy phenylene unit could form an enantiomeric smectic phase, but the remaining compounds with bent-core mesogenic unit were not liquid crystalline. In this presentation, their x-ray measurement and electro-optical property will be also described.

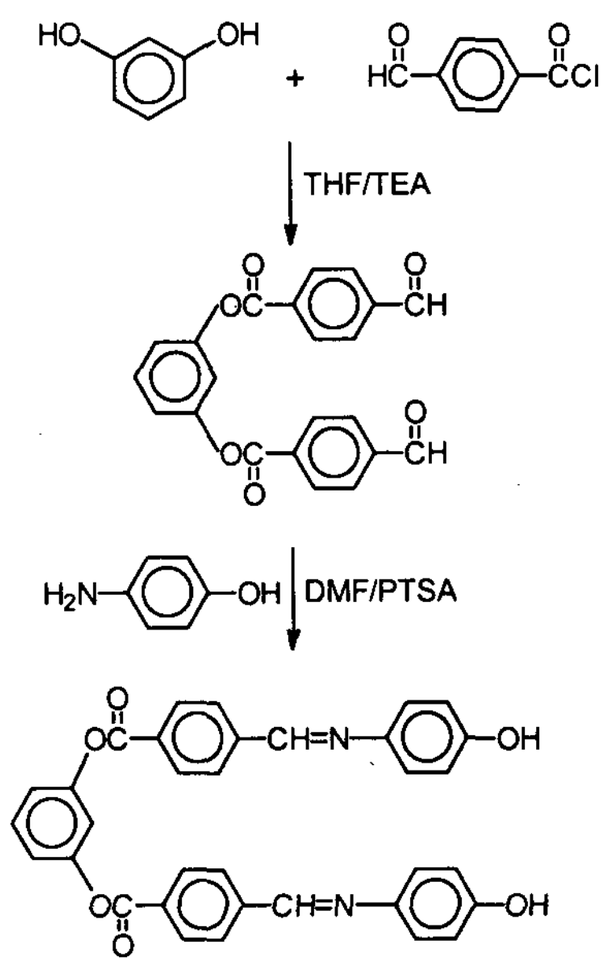
1. Introduction

Chirality has been accepted as the essential requirement for the smectic phase to show ferroelectricity [1], because the charity can reduce the overall symmetry of the smectic phase. However, in case that other structural factor would decrease the symmetry of the liquid crystal phase in the same manner as chirality, ferroelectricity could appear even in liquid crystal systems with non-chirality.

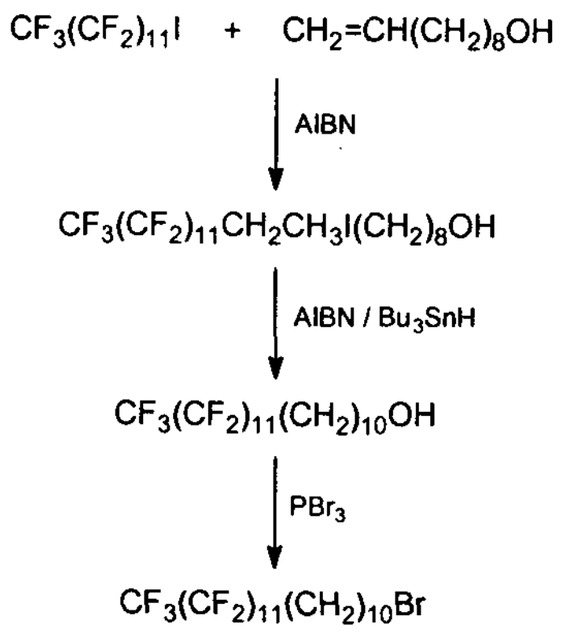
In 1993, Tournilnac et al. [2] reported that the synthesis and properties of new mesomorphic ferroelectrics composed of non-chiral polyphilic molecules. These polyphilic compounds consisted of a biphenyl rigid core and two semi-fluorinated alkyl chains. This is the first time that a ferroelectric repolarizable mesophase is obtained with non-chiral molecular units.

In 1996, Niori et al. [3] have observed the first obvious example of ferroelectricity in a smectic phase formed by achiral banana-shaped molecules, which consist of a central angular unit and two linear mesogenic units attached a terminal flexible chain. The bent-shaped molecules are tightly packed and are all aligned in the bent direction forming polar order. Link et al. [4] reported that achiral molecules with bent cores could form a chiral layer structure and the mesophase exhibited antiferroelectric phase. Sekine et al. [5, 6] reported that achiral banana-shaped molecule system could form helical domains in the smectic phases. We have also reported that synthesis and mesomorphic and elecreo-optical properties of banana-shaped molecules having lateral halogen substituent in the 3-position of p-alkoxyaniline Schiff's base moiety [7, 8].

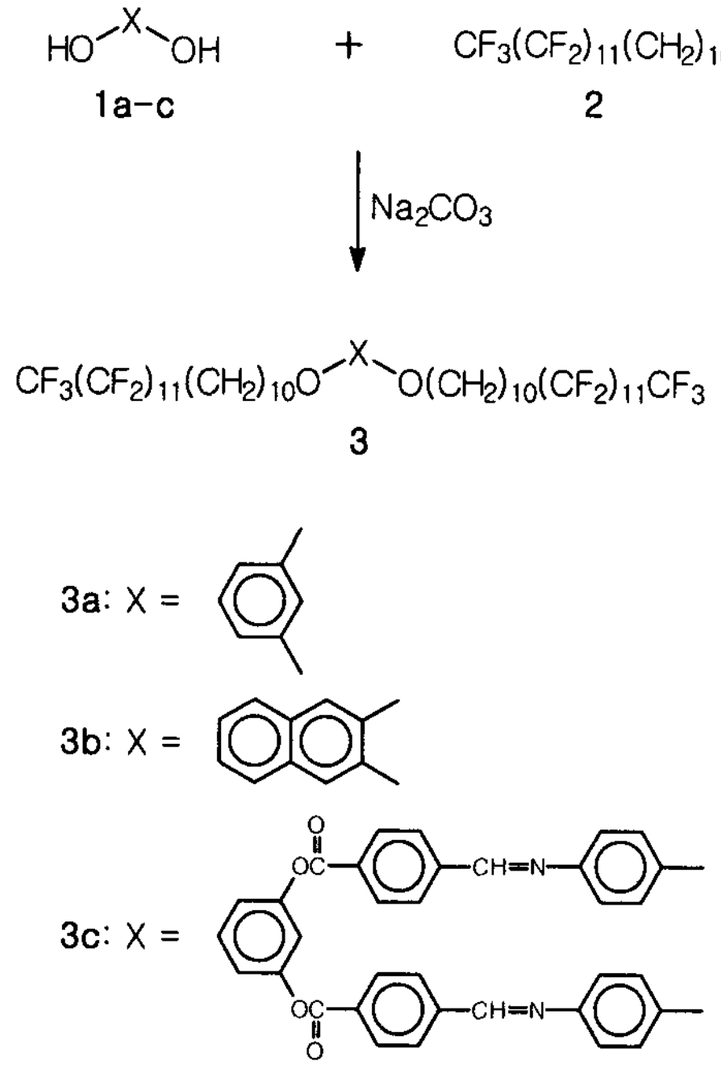
In this study, we describe synthesis and mesomorphism of non-conventional liquid crystalline compounds having bent-core mesogen and semi-fluorinated alkyl chains. Synthetic route to the compounds is shown in Schemes 1-3.



Scheme 1. Synthetic route to compound 1c.



Scheme 2. Synthetic route to compound 2.



Scheme 3. Synthetic route to compound 3.

2. Experimental

Since the synthetic procedures used to prepare the compounds were essentially same, one representative compound is given in the following.

2.1. Synthesis of compound 1c

Compound 1c was prepared using a modification of literature procedure [2] (see Scheme 1).

2.2. Synthesis of compound 2

Compound 2 was prepared according to details in the literature [7, 8] (see Scheme 2).

2.3. Synthesis of compound 3c

Into 10 mL of DMF were added compound 1c (0.036 g, 0.064 mmol), compound 2 (0.107 g, 0.13 mmol), and 0.12 g of Na_2CO_3. This reaction mixture was heated at 120℃ for 8 h with stirring under nitrogen atmosphere. After reaction, the mixture was poured into excess water, and the precipitated product was collected by filtering (see Scheme 3).

2.4. Characterization

IR and NMR spectra were obtained by a Jasco 300E FT/IR and Brucker DPX 200 MHz NMR spectrometers, respectively. The phase transition temperatures were determined by differential scanning calorimeter (duPont TA 910 DSC) and polarizing optical microscopy (Zeiss, Jenapol). DSC measurements were performed in a N_2 atmosphere. The DSC heating and cooling rates were of 10 °C/min. Optical textures were observed by a polarizing microscope equipped with a camera and a thermo-controller (Mettler FP82HT).

3. Results and Discussion

The synthetic routes for the compounds are rather straightforward as shown in Schemes 1-3. The obtained compounds were characterized by means of IR and NMR spectroscopy. IR and NMR spectral data were in accordance with expected formula. In Figure 1, all of the obtained compounds show the strong C-F absorption peak at 1200cm^{-1}.

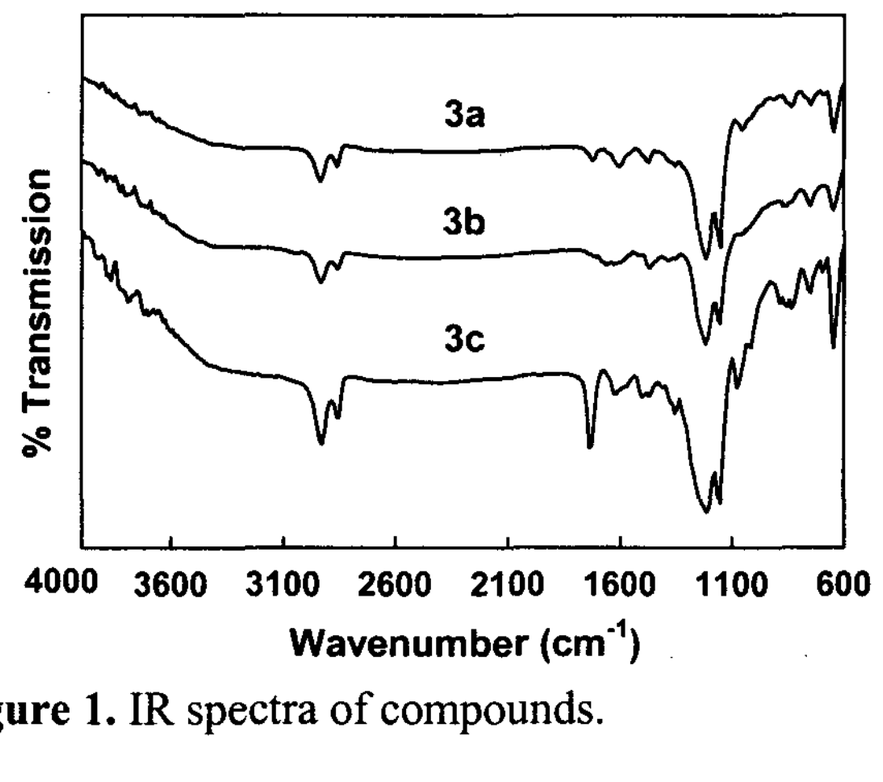


Figure 1. IR spectra of compounds.

DSC thermograms of the compounds are displayed in Figure 2. In the figure, compound 3a showed melting and isotropization transitions, while the rest of the

compounds showed only a melting transition. Tables 1 and 2 contain transition temperatures and changes of enthalpy for compounds. As you can see from the tables the compound 3a could form a mesophase reversibly, while the rest were not liquid cystalline. As shown in Figure 3, in the melt of the compound 3a a smectic optical texture was observed by a polarizing microscope.

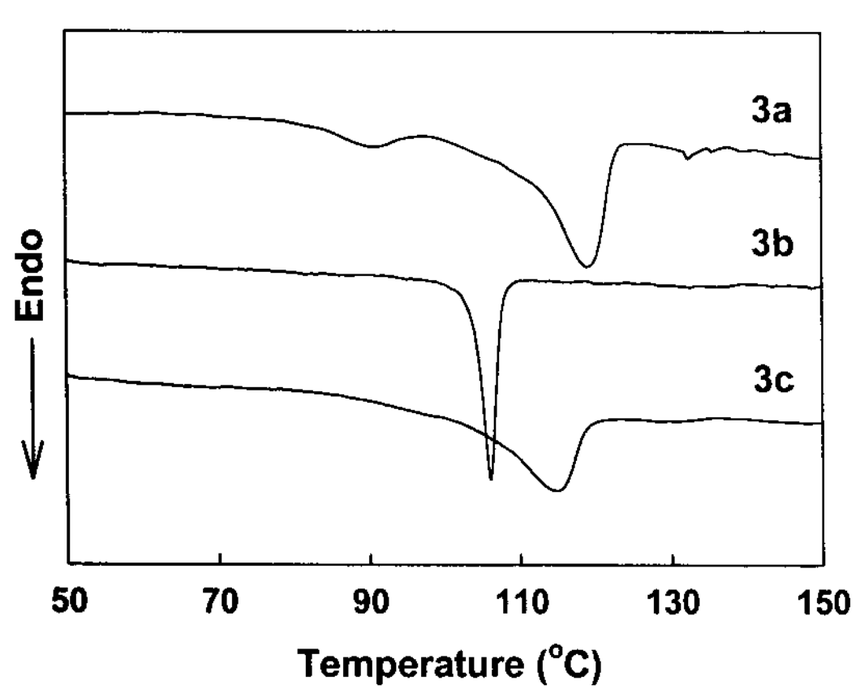


Figure 2. DSC thermograms of compounds.

Table 1. Melting temperatures (T_m) and corresponding enthalpy changes (ΔH_m) for compounds

Sample Code	T_m (°C)	ΔH_m (J/g)
3a	90.5	1.0
3b	106	7.7
3c	116	9.4

Table 2. Transition temperatures (°C) and corresponding enthalpy changes (in parenthesis, J/g) for compound 3a[a]

Heating		Cooling	
K-S	S-I	I-S	S-K
90.5	119.1	117.3	77.2
(1.0)	(7.0)	(13.3)	(1.2)

[a]Abbreviation: K = crystalline phase; S = smectic phase; I = isotropic phase.

This result indicates that compound 3c consisting of banana-shaped mesogenic unit could not help for semi-fluorinated alkyl group to form mesophase. When the naphthalene structure is too bent such as the compound 3b, the interchain interaction seems to be overruled by protrusion of 2,3-naphthalene group, and the compound could not liquid crystalline. On the contrary, compound 3a derived from resocinol, which has C_{2v} molecular symmetry, could form a smectic mesophase. More detailed studies to understand the structural effect of central unit are under way.

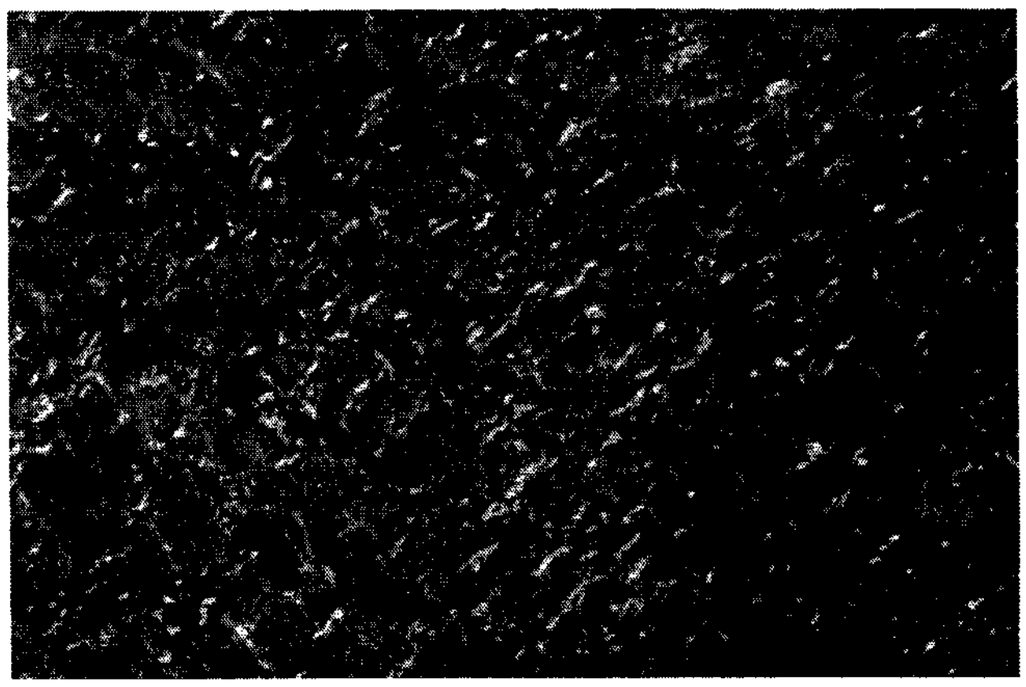


Figure 3. Polarizing optical micrograph of compound 3a taken at 67℃.

4. Acknowledgements

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5. References

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