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SYNTHESIS AND CHARACTERIZATION OF NEW LIQUID CRYSTALS CONTAINING A NON-ACTIVATED INDOLINOBENZOSPIROPYRANYL GROUP. PART 4*[1]

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A series of new liquid crystalline compounds, 1′,3′,3′-Trimethylspiro[2H-1-benzopyran-2,2′-indolin]-6-yl 4-(4′-alkoxyphenylazo)benzoate, **SP-APAB 1a ∼ 1f***, has been synthesized. Their liquid crystallines were subjected to thermal analysis on a differential scanning calorimeter (DSC), to texture of phases on a polarizing microscope and to phase transition on an X-ray diffraction and electro-optical measurement. Most of compounds examined exhibit monotropic nematic and SmA liquid crystal phases on cooling from isotropic liquid. Suprisingly,* **SP-APAB 1c** *is shown to exhibit monotropic SmC phase in addition. X-ray diffraction study of the layer spacing confirmed that there was a layer spacing in the range of two theta from 2.25 to 2.45 Å on the temperature near the phase transition from SmA to SmC.*

Keywords: indolinobenzospiropyran dye; liquid crystal optical switch; Nematic; Non-activated spiropyran; phase transition; Smectic A and Smectic C phase

INTRODUCTION

Photochromic materials [2,3] which can be reversibly written and read by light dominate the technology in our digital age. Organic photochromic compounds have obvious potential for such light-controlled devices.

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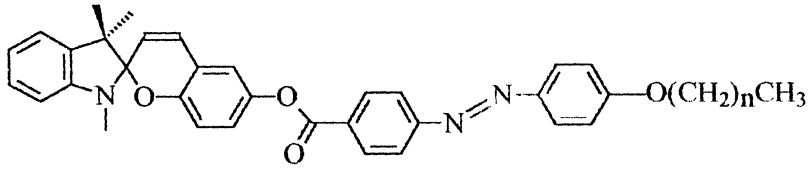
Among these materials, photochromic spiropyran dyes have attracted wide attention to many applications in optical switching, high-density optical data storage, holographic system and optical computing.

Although we have examined the synthesis and characterization of several series of liquid crystalline compounds containing a non-activated spiropyran unit as a chiral unit, a limited number of LC materials containing a non-activated spiropyran were found to exhibit a monotropic SmC phase [4,5]. These materials, exhibiting a SmC* phase after resolution, hold considerable potential as candidates for photo-resolvable dopants in UV-transparent nematic and polymeric nematic liquid crystal phases [6,7]. Irradiation of a suitable racemic chiral dopant in an aligned nematic liquid crystal with circularly polarized light would induce a cholesteric phase, whereas irradiation of the induced cholesteric phase with unpolarized light of the same wavelength would restore the nematic phase by photoracemization of the dopant. Because the light-induced interconversion between a spiropyran (SP)-an achiral merocyanine (MC) can be sensed by the change in the optical rotatory power of the liquid crystal, spiropyrans may serve as the basis for the liquid crystal optical switch. For the development of a liquid crystal optical switch (LCOS) based on the photoresolution [6], we have further expanded our research into SmC mesogens incorporating a non-activated spiropyran unit.

In this report we describe the synthesis and phase transition studies of a series of 1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl 4-(4′-alkyloxyphenylazo) benzoate, **SP-APAB 1a∼1f**.



SP-APAB **1a**, n=4; **1b**, n=5; **1c**, n=6; **1d**, n=7; **1e**, n=8; **1f**, n=9

MATERIALS AND EXPERIMENTAL METHODS

The DSC thermograms of the compounds were obtained using a DuPont 910 Thermal Analyzer calibrated with indium under N_2 atmosphere at a heating/cooling rate of 10℃ min^{-1}. The optical textures and thermal transitions were achieved using a Nikon Labophot-2 polarizing microscope equipped with a Mettler FP82HT hot stage. An X-ray diffractometer, 3kW-8eV, was applied for studying the phase transition on temperatures.

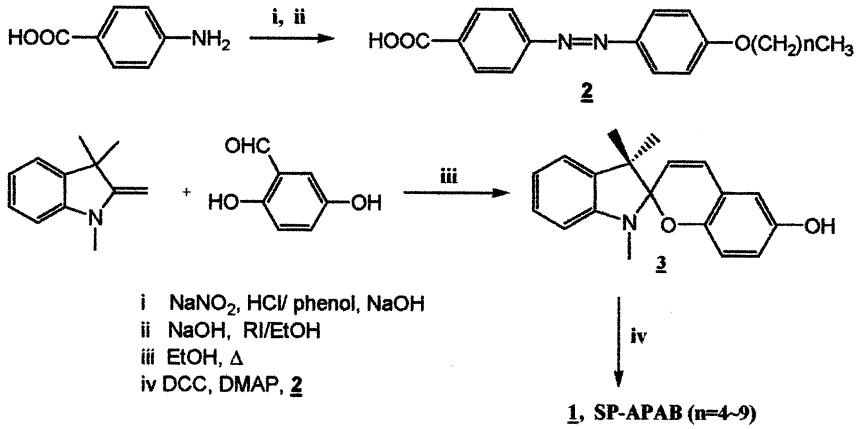
The bulk sample was aligned by slowly cooling from the isotropic phase in the presence of a ~2.5 kG magnetic field produced by a pair of rare-earth permanent magnets placed inside the oven. The x-ray scattering for phase transitions were performed on a 18-kW rotating anode source, and two-circle and four-circle goniometers with a pair of Ge(111) crystals used as monochromator and analyzer. The bulk sample was aligned slowly by cooling from the temperature at isotropic phase to the temperature at smectic phase in the presence of 50 kG strong magnetic field produced in the environment of liquid helium. The temperature was kept stable less than 5 mK. The temperature and data were controlled by computer using GPIB. The twisted nematic (TN) cell and the 4 micron cell with planar alignment were made by the general method by using a commercial align-materials, RN1199, whose pretilt angle was ~1. Two side 90° twisted rubbing and one side rubbing treatment were applied for the TN cell and 4 micron cell with planar alignment, respectively, and our compound filled slowly at the temperature of the isotropic phase. The thickness of the cell gap was controlled uniformly by a 4.5 μm spacer for optical study.

The detailed synthesis of these LC compounds will be published elsewhere [8].

RESULTS AND DISCUSSION

A series of new liquid crystalline compounds, 1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indolin]-6-yl 4-(4′-alkoxyphenylazo)benzoate, **SP-APAB 1a–1f** are synthesized in 48–71% yield via DCC esterification of 6-hydroxy-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indolin] **4** with the corresponding 4-(4′-alkoxyphenylazo)benzoic acid **3**. These 4-(4′-alkoxyphenylazo)benzoic acid **3** were obtained from a diazo coupling reaction of 4-aminobenzoic acid with sodium nitrite/HCl in the presence of phenol/NaOH, followed by alkylation in EtOH using the corresponding iodoalkanes**,** as shown in the Scheme 1.

The mesophase characterization of liquid crystal phases exhibited by **SP-APAB**were studied by differential scanning calorimeter (DSC), optical polarizing microscopy, the X-ray diffraction method and the electro-optical method. The DSC thermograms of **SP-APAB 1**a-**1f** exhibited a mesomorphic behavior on the first cooling and the subsequent cycle. Most of the compounds (except **1c**) formed both monotropic nematic and SmA phases, whereas **1c** formed a nematic, SmA and SmC phases, interestingly. From the DSC thermogram of **1c**, the first and second weak peak at 113 and 100℃ on cooling were identified to be a nematic and SmA phase, respectively. Upon lowering the temperature further, the next transition at 95℃ corresponding to the appearance of SmC phase was revealed.



SCHEME 1

The fourth strong peak at 90°C was found to be the crystal phase. Other compounds exhibited an isotropic→nematic→SmA phase sequence with decreasing temperature.

As a result of the polarizing microscopy study for **1c** showed a nematic, SmA and SmC phase on cooling from the isotropic phase, as shown in Figure 1.

In order to confirm the phases obtained by thermal fluctuation from DSC and by texture from optical microscopy for **SP-APAB 1e**, we used a normal twisted nematic (TN) cell with 4.5 μm cell gap and a 4 micron cell with planar alignment applied one side rubbing with the same cell gap. The TN cell showed the white state at 200℃ without voltage, but showed the black state at the same temperature with 15 V voltage. It can be understood a nematic

FIGURE 1 Optical textures of **1c**: (a) nematic phase at 113℃, (b) SmA phase at 99℃, (c) SmC phase at 97℃ on cooling; magnification 200x. (See COLOR PLATE III)

phase at 200℃. In the case of the 4 micron cell with planar alignment at 150℃, there was no change of transmittance even though we applied the electric field on the range of 0 ∼40 V/μm. It meant that molecular orientation was perpendicular to the layer, which indicated a SmA phase. When we rotated the cell at 150℃ without applying the electric field under the two crossed polarizers, the highest transmittance (white state) was from rotating 45° at angle of the black state. From these results, we confirmed this compound only has a SmA phase.

The SmC for **1c** was identified further by the X-ray diffraction method. Peak positions on three different temperatures were almost same which meant phase transition was not occurred yet, but intensity decreased when temperature decreased near the phase transition temperature because of starting the molecular fluctuations when phase will start to change as shown in Figure 2. There was only one layer spacing on these temperatures in the range of two theta from 2.25 to 2.45° and their peak position on two theta was 2.35° which could be concerned molecular length, 37.6 Å. The full width half maximum(FWHM) was very narrow and didn't change on these three temperatures. It indicated one of smectic phases. The similar results to confirm the phase transition was given in Figure 3 drawn the intensity against two theta on other three temperatures. At the SmA to the chiral smectic phase transition, the intensity and the layer spacing, which corre-

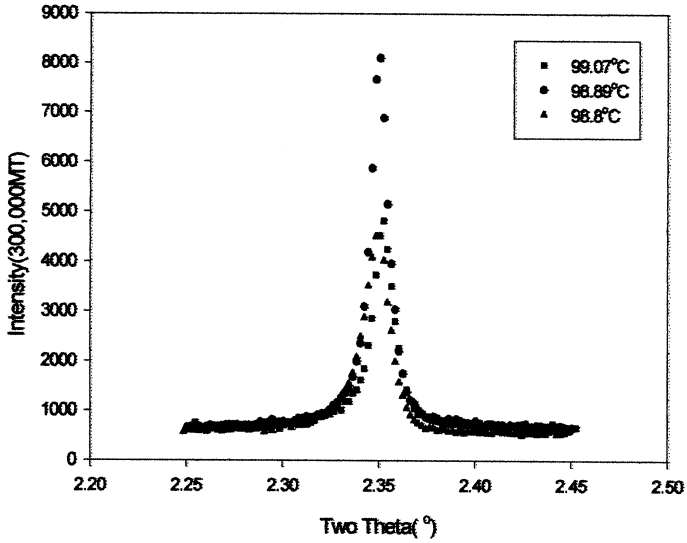


FIGURE 2 Intensity versus two theta on three different temperatures just above SmC phase.

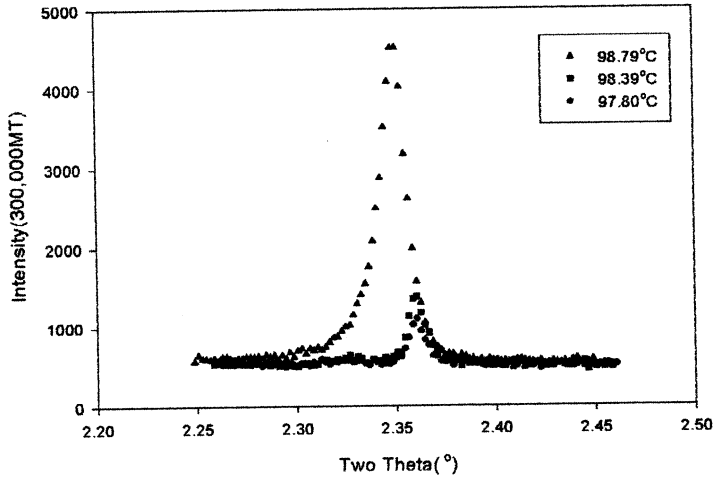


FIGURE 3 Intensity versus two theta on three different temperatures near temperature of the phase transition from SmA to the SmC.

sponded the peak position obtained by two theta scan, decreased as shown in Figure 3. The peak position at 98.79℃ was 2.35° on two theta scan which were same value obtained at the higher temperature, but the peak position at other two lower temperatures, 98.3 and 97.80℃, was each shifted to larger than 2.36, which gave a clue of molecular tilt to the layer and a tran-

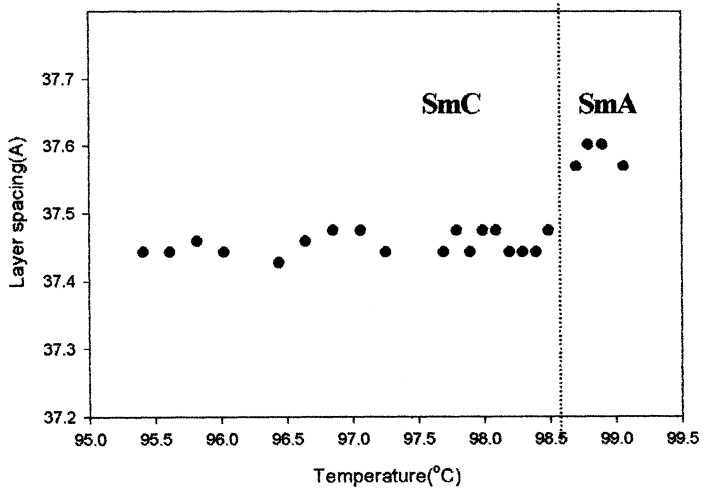


FIGURE 4 Layer spacing versus temperature.

TABLE 1 Phase Transition Temperatures of the Synthesized LC Compounds, **1a–1f**

	Cr		SmC		SmA		N		I
1a	•	103	–	–	•	117	•	128	•
1b	•	106	–	–	•	115	•	126	•
1c	•	95.3	•	98.5	•	100	•	113	•
1d	•	102	–	–	•	108	•	122	•
1e	•	62	–	–	•	105	•	118	•
1f	•	92	–	–	•	100	•	111	•

sition from SmA to SmC phase. Intensity at the these temperatures were almost constant because of finishing the molecular fluctuation which induced phase transition. Smectic layer spacing d calculated from Bragg condition, $2d \sin\theta = \lambda$; θ is angle of peak position on two theta scan and λ is wavelength to electromagnetic radiation of 8 keV quantum energy, is shown in Figure 4 as a function of temperature. The value of d obtained in a particular run did not depend on sample history and on the time spent at any temperature. The behavior of d and phase change in the two smectic regions is in quantitative agreement with the other results. Figure 4 showed a phase transition from smectic A (SmA) to chiral smectic (SmC) at $\sim$98.6℃ which was the temperature occurred an abrupt change on layer spacing due to molecular tilt to the layer. The layer spacing d below 98.5℃ which is region of SmC phase, is quite constant. The tilt angle at the chiral smectic phase is $\sim$5 degree. Since this tilt angle is quiet small, one could say that it may be a smectic C phase.

It was found that a few compounds exhibited the enantiotropic nematic phase by repeated measurements. Regardless of chain length, most compounds examined in this study were transformed to amorphous solids which slowly recrystallized at room temperature within a few hours to several days. The transition temperatures and the phases for **ABP-SPAB 1a**$\sim$**1f**(n=4$\sim$9) are given in Table 1.

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