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Synthesis and characterization of new liquid crystallines containing a mono-aza styrylated indolinobenzospiropyran. Part 6[☆]

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Abstract

A series of new liquid crystalline compounds containing a mono-aza styrylated indolinobenzospiropyran, **1a**–**1d**, has been synthesized. The synthesized LC dyes are subjected to thermal analysis on a differential scanning calorimeter (DSC), to texture of phases on a polarizing microscope and electro-optical system. All compounds examined in the series are monotropic and have relatively low mp's (125–128 °C). Nematic liquid crystal phases are detected both on cooling from isotropic liquid and on heating from crystal of the LC compounds.

Keywords: Spiropyran-containing liquid crystal; Mono-aza styrylated indolinobenzospiropyran; Enantiotropic; Photochromic dye; Nematic liquid crystals; DSC thermal analysis

1. Introduction

Thermo- and photochromic indolinobenzospiropyran dyes recently have become important in connection with the rapid development of information recording systems, high-density optical data storage, displays, holographic devices and as optical switches [1–2].

Spiropyran (SP) is inherently a chiral compound that undergo a reversible photochemical ring opening to give achiral merocyanine (MC) [3–11]. When irradiated with unpolarized light, the prochiral MC undergoes ring closure to form (R)-SP of (S)-SP at equal rates and under such conditions of the photostationary state, the SP exists as rapidly interconverting enantiomers [12]. Photochromic SP-liquid crystal materials hold thus considerable potential as candidates for photoresolvable dopants in UV-transparent nematic and polymeric nematic liquid crystal phases. Chiral liquid crystals that contain an asymmetric atom can produce chiral mesophases. These can selectively reflect visible light or sometimes exhibit ferroelectricity. Ferroelectric liquid crystals are of considerable interest for use in fast optical light shutters and for the liquid crystal optical switch(LCOS) [13–15].

In this connection, we have recently expanded our research into various mesogens incorporating

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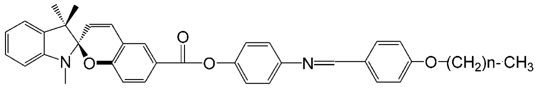
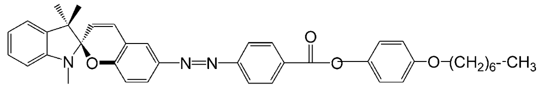
a spiropyranyl group [8–11,15,16]. Those LC molecules are expected to have the chiroptical properties essential for the liquid crystal optical switch. In this report we describe a study of new liquid crystalline compounds containing a mono-aza styrylated indolinobenzospiropyran, **1a**–**1d**, comparing to those of LC molecules, **2,** reported previously [10].



1a; n=4, **1b**; n=5, **1c**; n=6, **1d**; n=7



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2. Experimental

2.1. General

Melting points were determined using a Fischer–Jones melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained in DMSO-d_6 on a Varian 300 NMR spectrophotometer. Chemical shifts were reported in δ (ppm) relative to tetramethylsilane as the internal standard. High-resolution FAB mass spectra were obtained by the Basic Science Research Institute, korea University at Seoul Campus. 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 °C min^{-1}. The optical textures and thermal transitions were achieved using a Nikon Labophot-2 polarizing microscope equipped with a Mettler FP82HT hot stage. The twisted nematic (TN) cell and the 4 μM 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 μM 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.

2.2. Materials

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. Dichloromethane was distilled from calcium hydride prior to use. 5-Carboxy-2-hydroxybenzaldehyde was prepared by formylation of hydroxybenzoic acid via a Reimer-Tiemann reaction. The alkoxybenzaldehydes were prepared by the procedure of Gray et al. [17]. 6-Carboxy-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] was prepared by condensation of 2-methylene-1,3,3,-trimethylindoline (Fischer's base) with 5-Carboxy-2-hydroxybenzaldehyde, using the known procedure of Keum et al. [4].

2.2.1. Synthesis of 4-(4′-alkyloxyphenylimino)-phenol *3*

To a solution of 4-alkoxybenzaldehyde (16.1 mmol) in 100 ml of acetonitrile, 4-aminophenol (1.76 g, 16.1 mmol) was added, which was stirred for 12 h at room temperature. After the reaction was complete, it was filtered and washed with acetone. Recrystalization from acetone gave the light-gray coloured material **3,** for example, **3a**; (mp 148 °C, yield 76%) ^{1}H NMR (300 MHz, DMSO) δ 0.90 (t, 3H), δ 1.29–1.42 (m, 4H), δ 1.74 (m, 2H), δ 4.03 (t, 2H), δ 6.76 (d, 2H), δ 7.03 (d, 2H), δ 7.14 (d, 2H), δ 7.81 (d, 2H), δ 8.50 (d, 1H).

2.2.2. Synthesis of 5-carboxy-2-hydroxybenzaldehyde

To a solution of sodium hydroxide (2.61 g, 65.1 mmol) in 20 ml of water, 4-hydroxybenzoic acid (3 g, 21.7 mmol) and $CHCl_3$ (7.77 g, 65.1 mmol) were added, which was stirred for 5 h at 60 °C. After the reaction was complete, the solution was acidified by diluted HCl. The solvent was removed in vaccuo yielding 1.61 g of crude product.

2.2.3. Synthesis of 6-carboxy-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] *4*

To a solution of 5-carboxy-2-hydroxybenzaldehyde (1 g, 6.0 mmol) in 100 ml ethanol, Fischer's base (0.73 g, 4.2 mmol) was added, which was stirred for 6 h. After the reaction was complete, the solvent was removed in vaccuo. The product was purified by column chromatography on silica-gel (EtOAc 5%–hexane 95%, v/v%). The solvent was removed in vaccuo yielding 1.35 g of pale-pink product, (mp 199 °C, yield 70%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 3H), δ 1.31 (s, 3H), δ 2.75 (s, 3H), δ 5.77 (d, 1H), δ 6.56 (d, 1H), δ 6.76 (d, 1H), δ 6.88 (t, 1H), δ 6.93 (d, 1H), δ 7.09 (d,1H), δ 7.20 (t, 1H), δ 7.86 (s, 1H), δ 7.88 (t, 1H).

2.2.4. *General procedure for the esterification of compounds **3** and **4***

The following procedure is representative. To a solution of **3** 4-(4′-pentyloxyphenylimino)phenol (1 g, 3.2 mmol) in 100 ml of methylene chloride and **4** 6-carboxy-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (1.03 g, 3.2 m mol) were added *N,N′*-dicyclohexylcarbodiimide (DCC, 0.78 g, 3.8 mmol) and 4-dimethylaminopyridine (DMAP, 0.05 g, 0.4 mmol). The mixture was stirred at room temperature and monitored by TLC until completion of the reaction. The solvent was removed in vaccuo, and the ester purified by column chromatography on silica-gel (EtOAc 5%-hexane 95%, v/v%). Recrystalization from acetone gave the product **1**.

*2.2.4.1. 4″-(4‴-Pentyloxyphenylimino)phenyl-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl carboxylate **1a***. Yield 21%, mp 125 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H), δ 1.20 (s, 3H), δ 1.33 (s, 3H), δ 1.35–1.52 (m, 4H), δ 1.83 (m, 2H), δ 2.76 (s, 3H), δ 4.03 (t, 2H), δ 5.79 (d, 1H), δ 6.57 (d, 1H), δ 6.81 (d, 1H), δ 6.88 (t, 1H), δ 6.95 (d, 1H), δ 6.98 (d, 2H), δ 7.10 (d, 1H), δ 7.19 (t, 1H), δ 7.20 (d, 2H), δ 7.25 (d, 2H), δ 7.84 (d, 2H), δ 7.95 (s, 1H), δ 7.98 (d, 1H), δ 8.40 (s, 1H). High-resolution MS: calculated for $C_{38}H_{38}N_2O_4$ 586.2832; found 586.2859.

*2.2.4.2. 4″-(4‴-Hexyloxyphenylimino)phenyl-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl carboxylate **1b***. Yield 20%, MP 128 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H), δ 1.20 (s, 3H), δ 1.33 (s, 3H), δ 1.35–1.54 (m, 6H), δ 1.82 (m, 2H), δ 2.76 (s, 3H), δ 4.03 (t, 2H), δ 5.79 (d, 1H), δ 6.57 (d, 1H), δ 6.81 (d, 1H), δ 6.88 (t, 1H), δ 6.95 (d, 1H), δ 6.98 (d, 2H), δ 7.09 (d, 1H), δ 7.19 (t, 1H), δ 7.19 (d, 2H), δ 7.25 (d, 2H), δ 7.84 (d, 2H), δ 7.95 (s, 1H), δ 7.98 (d, 1H), δ 8.40 (s, 1H). High-resolution MS: calculated for $C_{39}H_{40}N_2O_4$ 600.2988; found 600.2899.

*2.2.4.3. 4″-(4‴-Heptyloxyphenylimino)phenyl-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl carboxylate **1c***

Yield 25%, MP 125 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H), δ 1.20 (s, 3H), δ 1.33 (s, 3H), δ 1.34–1.59 (m, 8H), δ 1.82 (m, 2H), δ 2.76 (s, 3H), δ 4.03 (t, 2H), δ 5.79 (d, 1H), δ 6.57 (d, 1H), δ 6.81 (d, 1H), δ 6.88 (t, 1H), δ 6.95 (d, 1H), δ 6.98 (d, 2H), δ 7.10 (d, 1H), δ 7.19 (t, 1H), δ 7.19 (d, 2H), δ 7.25 (d, 2H), δ 7.84 (d, 2H), δ 7.95 (s, 1H), δ 7.98 (d, 1H), δ 8.40 (s, 1H). High-resolution MS: calculated for $C_{40}H_{42}N_2O_4$ 614.3145; found 614.3168.

*2.2.4.4. 4″-(4‴-Octyloxyphenylimino)phenyl-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline]-6-yl carboxylate **1d***. Yield 19%, MP 128 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H), δ 1.20 (s, 3H), δ 1.32 (s, 3H), δ 1.29–1.55 (m, 10H), δ 1.81 (m, 2H), δ 2.76 (s, 3H), δ 4.03 (t, 2H), δ 5.79 (d, 1H), δ 6.57 (d, 1H), δ 6.81 (d, 1H), δ 6.88 (t, 1H), δ 6.95 (d, 1H), δ 6.98 (d, 2H), δ 7.10 (d, 1H), δ 7.19 (t, 1H), δ 7.19 (d, 2H), δ 7.25 (d, 2H), δ 7.84 (d, 2H), δ 7.95 (s, 1H), δ 7.98 (d, 1H), δ 8.40 (s, 1H). High-resolution MS: calculated for $C_{41}H_{44}N_2O_4$ 628.3301; found 628.3324.

3. Results and discussions

3.1. *Synthesis*

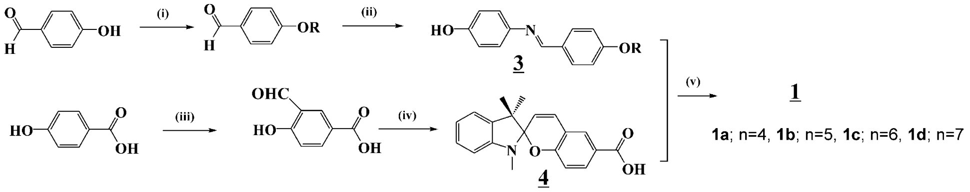
A series of new liquid crystalline compounds containing a mono-aza styrylated indolinobenzospiropyran, **1a–1d**, have been synthesized via DCC esterification of 6-carboxy-1′,3′,3′-trimethylspiro [2H-1-benzopyran-2,2′-indoline] **4** with the corresponding 4-(4′-alkyloxyphenylimino)phenol **3**. The carboxylated spiropyrans **4** was readily obtained by reaction of the corresponding salicylaldehydes with 2-methylene-1,3,3-trimethylindoline (Fischer's base) [15]. The 4′-alkyloxybenzaldehydes were obtained from alkylation reaction of 4-hydroxybenzaldehyde in EtOH using the corresponding iodoalkanes. The synthetic processes are shown in the Scheme 1.

3.2. Mesophase characterization

The mesophase characterization of liquid crystal phases exhibited by the LC compounds prepared have been investigated by polarizing optical microscopy (POM), and the phase transition temperatures were confirmed by differential scanning calorimeter (DSC) and the electro-optical method. The polarizing optical microscopy study for **1a**–**1d** showed nematic phases on cooling from the isotropic phase, as evidenced by the schlierene textures observed by POM [18–19]. These are shown in Fig. 1. Unfortunately, none of the esters formed Sm phase, which we were aiming for.

From the DSC thermogram obtained from the compounds, **1a–1d**, mesomorphic behavior on the first cooling and the subsequent cycle were confirmed. All of the ester derivatives reported herein formed a monotropic mesophase. As an example of the DSC thermogram obtained from **1b**, the peak at 123.2 °C on cooling were identified to be a nematic phase. Upon lowering the temperature further, the next transition was not revealed. This strong peak was found to be the crystal phase at 60.0 °C. Other compounds also exhibited an isotropic→nematic→crystal phase sequence with decreasing temperature.

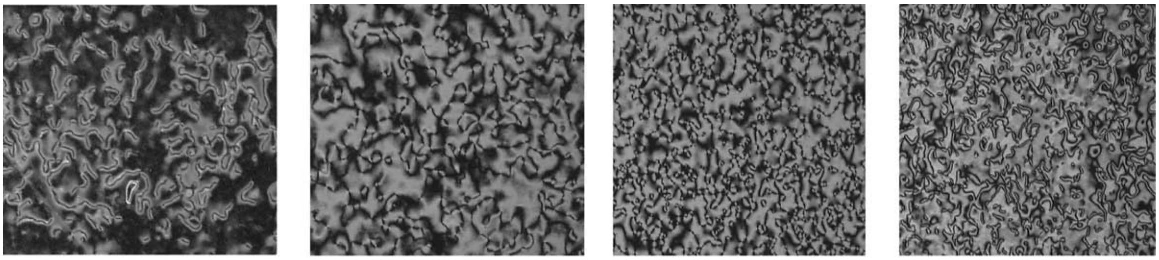
In order to confirm further the phases obtained by thermal fluctuation from DSC and by texture from optical microscopy for **1b**, we used a normal twisted nematic (TN) cell with 4.5 μm cell gap and a 4 micron cell with planar alignment applied one side rubbing with the same cell gap. The TN cell showed the white state at 120 °C without voltage, but showed the black state at the same temperature with 15 V voltage. It can be understood a nematic phase at 120 °C. 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



(i) RI , K_2CO_3 / CH_3CN (reflux), (ii) 4- Aminophenol / CH_3CN, (iii) $CHCl_3$, NaOH / H_2O , 60°C

(iv) Fischer's base / EtOH, (v) DCC , DMAP / CH_2Cl_2

Scheme 1.



a) **1a** at 108.8°C b) **1b** at 123.2°C c) **1c** at 109.4°C d) **1d** at 96.9°C

Fig. 1. Optical textures of nematic phases of **1a**–**1d** on cooling; magnification 200×.

Table 1
Transition temperatures of mono-aza styrylated spirobenzopyrans on cooling from isotropic liquid

Compd.	I		N	SmA		Cr	Note
1a	•	124	•	—		•	This work
1b	•	124	•	—		•	This work
1c	•	110	•	—		•	This work
1d	•	114	•	—		•	This work
2 (*n* = 6)	•	99	•	—	72	•	Ref. [10]

and the phases for **1a–1d** are shown in Table 1. For the comparison, phase transition temperatures of other LC materials (**2**) are included.

It has been known that linking groups are those structural units that connect one part of a core to another. To be successful in facilitating liquid crystal phase generation, linking groups must maintain the linearity of the core and be compatible with the rest of the structure. Traditionally, linking groups are used to extend the length and polarizability anisotropy of the molecular core in order to enhance the liquid crystal phase stability by more than any increase in melting point, producing wider liquid crystal phase ranges. From this work and our previous results, we observed that the liquid crystal phase stability decreases in order of Series **2**–Series **1**. Series **1**–Series **2** are very similar structurally. The fine structural differences of the two compounds results in entirely different LC phases. Series **1** has an imine double bond as a mesogen between two phenyl groups, whereas Series **2** have an azo double bonds, although the connecting sequences are different. This structural difference may enhance polarisability anisotropy of the molecular core and hence enhance the liquid crystal phase stability. This result implies that substitution of a OCO linkage for the COO linking group in this Series **1** is expected to enhance the liquid crystal phase stability. Further work aimed at developing photostable spiropyran-containing Sm mesogens is in progress.

Acknowledgements

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