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Synthesis and characterization of new liquid crystallines containing a thiophenylated indolinobenzospiropyranyl group. Part 5☆

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Abstract

A series of new liquid crystalline compounds containing a thiophenylated 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 these series are enantiotropic and have relatively low m.p.s. Nematic liquid crystal phases are detected both on cooling from isotropic liquid and on heating from crystal of the series.

Keywords: Liquid crystal; Thiophenylated indolinobenzospiropyran; Photochromic dye

1. Introduction

Photochromic materials are highly versatile molecules that find application in a range of variable transmission devices in the opthalmics, automotive and architectural industries. Selected hi-tech uses include their incorporation into high-density optical data storage, displays, photovoltaic, holographic devices and as optical switches [2,3] Thermo- and photochromic indolinobenzospiropyran dyes recently have become important in connection with the rapid development of information recording systems, Spiropyran (SP) is inherently a chiral compound that undergo a reversible photochemical ring opening to give achiral merocyanine (MC). [4–12] 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 [13].

Photochromic SP-liquid crystal materials hold considerable potential as candidates for photoresolvable dopants in UV-transparent nematic and polymeric nematic liquid crystal phases. 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. In order to induce a

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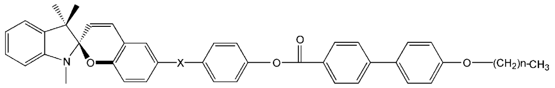
nematic-cholesteric phase transition via the photoresolution of the SP dopant, it is important that the photostationary state concentration of the SP-MC pair favors the SP component. Chiral liquid crystals that contain an asymmetric atom can produce chiral mesophases. These can selectively reflect visible 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) [14–16].

We have thus recently expanded our research into other mesogens incorporating a spiropyranyl group, 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 thiophenylated indolinobenzospiropyran, **1a–1d**, comparing to those of LC molecules, **2–4**, reported previously.



X= S (1), CO (2), -N=N- (3), - (4)
1a; n=6, **1b**; n=7, **1c**; n=8, **1d**; n=9

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 ä(ppm) relative to tetramethylsilane as the internal standard. High-resolution FAB mass spectra were obtained by the Basic Science Research Institute [17]. 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 μ 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.

2.2.1. 3-(p-Hydroxyphenylsulfanyl)salicylaldehyde (5)

To a solution of 4,4′-thiodiphenol (3 g, 13.6 mmol) in 100 ml toluene was added $SnCl_4$ (0.35 ml, 2.99 mmol) and tributylamine (2.59 ml, 10.9 mmol) under N_2 at room temperature. After refluxing the reaction mixture for 30 min, paraformaldehyde (2.06 g, 65.3 mmol) was added under N_2 atmosphere and the mixture refluxed for 8 hrs. At the end of reaction, solution was neutralized with 2 M HCl. The solution was extracted with EtOAc, dried with $MgSO_4$ and finally concentrated in vacuo. Flash chromatography (EtOAc 20%–hexane 80%, v/v%) and recrystallization from acetone afforded 1.38 g (41%) of yellow solid, 5 m.p. 97 °C (lit. [12] 97–98 °C).

2.2.2. 6-(p-Hydroxyphenylsulfanyl)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (6)

To a solution of 3-(*p*-hydroxyphenylsulfanyl)-salicylaldehyde (2.0 g, 4.98 mmol) in 20 ml of EtOH Fischer's base (0.8 g, 4.6 mmol) was added. The mixture was stirred for 12 h at room temperature. After the reaction was complete, the mixture was then poured into 100 ml of distilled water and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. The recrystallization from ethyl acetate/hexane (1:10) gave 3.4g as marine blue crystal. Yield 65%. M.p. 72 °C (lit. [12] 71–72 °C).

2.2.3. 4′-Alkyloxy-4-biphenylcarboxylic acid (7)

The following procedure is representative. To a 4′-hydroxy-4-biphenylcarboxylic acid (1.0 g, 4.67 mmol) in 60 ml of EtOH, NaOH (0.4 g) was added and the mixture was refluxed. After 30 min, iodononane (0.24 ml, 1.34 mmol) was added to this solution and refluxed again for 16 h. The remaining solid was filtered and the filtrate was neutralized with dil. HCl, evaporated in vacuo and extracted with methylene chloride. The recrystallization from EtOH gave white crystal, **7c**. Yield 58%. M.p. 161 °C (lit. [12] 161–162 °C).

*2.3. General procedure for the esterification of **6***

The following procedure is representative. To a solution of 4′-alkyloxy-4-biphenylcarboxylic acid (0.32 mmol) and solution of **6** (0.19 g, 0.47 mmol) in 20 ml of dried CH_2Cl_2 were added 1,3-dicyclohexylcarbodiimide (DCC, 0.11 g, 0.56 mmol) and 4-dimethylaminopyridine (DMAP, 0.03 g, 0.22 mmol). The mixture was stirred at room temperature and monitored by the TLC pattern until completion of the reaction. The solvent was removed in vacuo, and the ester was purified by column chromatography on silica gel (20:1 hexane/ethyl acetate) which gave white solid, **1e**. The product was further purified by recrystallization from acetone.

*2.3.1. [6″-(1⁗-Phenylsulfanyl)-1‴,3‴,3‴,-trimethyl-spiro(2″H-1″-benzopyran-2″,2‴-indoline)-4⁗-yl]-4′-heptyloxy-4-biphenylcarboxylate **1a***

Yield 54%. M.p. 85 °C. ^{1}H NMR (300 MHz, DMSO) δ 0.87 (t, 3H), 1.10 (s, 3H), 1.23–1.42 (m, 8H), 1.28 (s, 3H), 1.73 (m, 2H), 2.67 (s, 3H), 4.02 (t, 2H), 5.85 (d, J = 10.2Hz, 1H), 6.58 (d, J = 7.7Hz, 1H), 6.77 (d, 1H), 6.78 (t, 1H), 7.04 (d, 1H), 7.07 (d, 2H), 7.08 (d, 1H), 7.11 (t, 1H), 7.21 (d, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.28 (s, 1H), 7.41 (d, 2H), 7.73 (d, J = 8.7 Hz, 1H), 7.86 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 9.0 Hz, 2H). High resolution MS: calculated for $C_{45}H_{45}NO_4S$; 695.9091; found 695.9096.

*2.3.2. [6″-(1⁗-Phenylsulfanyl)-1‴,3‴,3‴-trimethyl-spiro(2″H-1″-benzopyran-2″,2‴-indoline)-4⁗-yl]-4′-octyloxy-4-biphenylcarboxylate **1b***

Yield 61%, m.p. 76.5 °C. ^{1}H NMR (300 MHz, DMSO) δ 0.87 (t, 3H), 1.10 (s, 3H), 1.23–1.43 (m, 10H), 1.27 (s, 3H), 1.73 (m, 2H), 2.67 (s, 3H), 4.03 (t, 2H), 5.86 (d, J = 10.2 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 6.78 (d, 1H), 6.81 (t, 1H), 7.05 (d, 1H), 7.08 (d, 2H), 7.09 (d, 1H), 7.11 (t, 1H), 7.22 (d, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.29 (s, 1H), 7.41 (d, 2H), 7.74 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 8.7 Hz, 2H), 8.16 (d, J = 9.0Hz, 2H). High resolution MS: calculated for $C_{46}H_{47}NO_4S$; 709.9357; found 709.9349.

*2.3.3. [6″-(1⁗-Phenylsulfanyl)-1‴,3‴,3‴-trimethyl-spiro(2″H-1″-benzopyran-2″,2‴-indoline)-4⁗-yl]-4′-nonyloxy-4-biphenylcarboxylate **1c***

Yield 56%, m.p. 79.0 °C. ^{1}H NMR (300 MHz, DMSO) δ 0.85 (t, 3H), 1.10 (s, 3H), 1.23–1.42 (m, 12H), 1.26 (s, 3H), 1.73 (m, 2H), 2.67 (s, 3H), 4.02 (t, 2H), 5.85 (d, J = 10.2 Hz, 1H), 6.59 (d, J = 7.9 Hz, 1H), 6.78 (d, 1H), 6.81 (t, 1H), 7.04 (d, 1H), 7.07 (d, 2H), 7.08 (d, 1H), 7.11 (t, 1H), 7.22 (d, 2H), 7.25 (d, J = 8.5 Hz 2H), 7.28 (s, 1H), 7.41 (d, 2H), 7.74 (d, J = 9.0 Hz, 1H), 7.87 (d, J = 8.6 Hz, 2H), 8.16 (d, J = 9.0 Hz, 2H). High resolution MS: calculated for $C_{47}H_{49}NO_4S$; 723.9623; found 723.9625.

*2.3.4. [6″-(1⁗-Phenylsulfanyl)-1‴,3‴,3‴-trimethyl-spiro(2″H-1″-benzopyran-2″,2‴-indoline)-4⁗-yl]-4′-decyloxy-4-biphenylcarboxylate **1d***

Yield 59%, m.p. 65.0 °C. ^{1}H NMR (300 MHz, DMSO) δ 0.85 (t, 3H), 1.10 (s, 3H), 1.23–1.41 (m, 14H), 1.25 (s, 3H), 1.73 (m, 2H), 2.67 (s, 3H), 4.02 (t, 2H), 5.85 (d, J = 10.3 Hz, 1H), 6.59 (d, J = 7.8 Hz, 1H), 6.78 (d, 1H), 6.80 (t, 1H), 7.04 (d, 1H), 7.07 (d, 2H), 7.08 (d, 1H), 7.11 (t, 1H), 7.21 (d, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.28 (s, 1H), 7.41 (d, 2H), 7.73 (d, J = 8.7 Hz, 1H), 7.87 (d, J = 8.7 Hz, 2H), 8.15 (d, J = 9.0 Hz, 2H). High resolution MS: calculated for $C_{48}H_{51}NO_4S$; 737.9889; found 737.9886.

3. Results and discussions

3.1. Synthesis

A series of new liquid crystalline compounds containing a thiophenylated indolinobenzospiropyran, **1a–1d**, has been synthesized in 54–61%

yield via DCC esterification of 6-(p-hydroxyphenylsulfanyl)-1′,3′,3′-trimethyspiro[2H-1-benzopyran-2,2′-indoline], **6** with the corresponding 4′-alkyloxy-4-biphenylcarboxylic acid, **7**. The substituted spiropyrans 6 was readily obtained by reaction of the corresponding salicylaldehydes with 2-methylene-1,3,3-trimethylindoline (Fischer's base) [16]. The 4′-alkyloxy-4-biphenylcarboxylic acids were obtained from alkylation reaction of 4-(4′-alkyloxy)benzoic acid in EtOH using the corresponding iodoalkanes, as shown in Scheme 1.

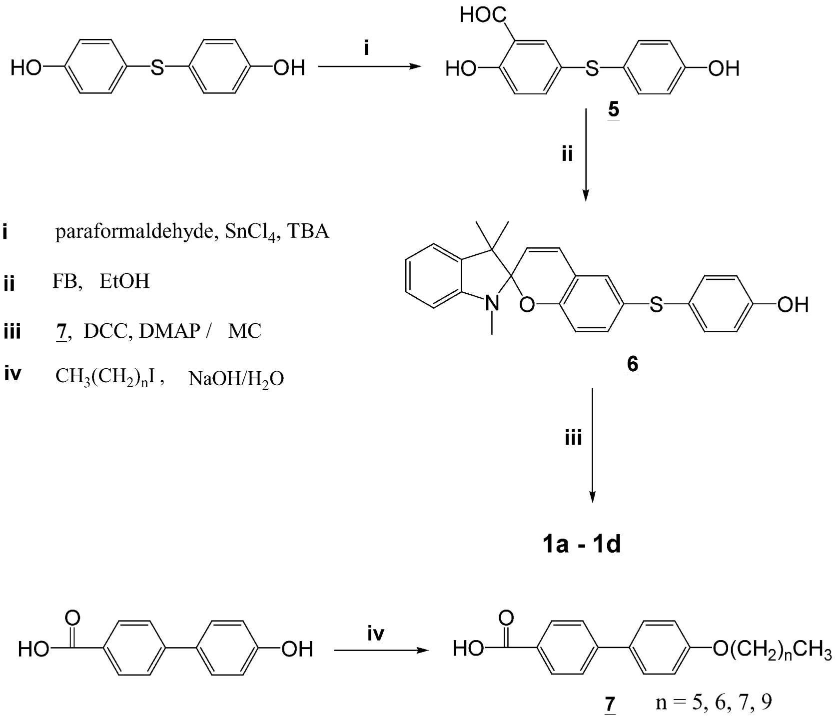
3.2. Mesophase characterization

The mesophase characterization of liquid crystal phases exhibited by the LC compounds prepared were studied by differential scanning calorimeter (DSC), optical polarizing microscopy and the electro-optical method.

The polarizing microscopy study for **1b–1d** showed nematic phases only both on cooling from the isotropic phase and on heating from crystal, as shown in Fig. 1. Surprisingly, **1a** which has the shortest alkylchain ($n=6$) among these series doesn't show any mesomorpic phases at all. None of the series examined showed either the schlieren or fan textures in polarizing microscopy [18–20]

From the DSC thermogram obtained from the compounds, **1b–1d**, mesomorphic behavior on the first cooling and the subsequent cycle were confirmed. All of the compounds (**1b–1d**) formed enantiotropic nematic phases. As an example of the DSC thermogram obtained from **1b**, the first peak at 74.9 °C on cooling were identified to be a nematic phase. Upon lowering the temperature further, the next transition at 70.5 °C was revealed. This strong peak was found to be the crystal phase. The DSC thermogram is shown in Fig. 2. 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 μ cell with planar alignment applied one side



Scheme 1.

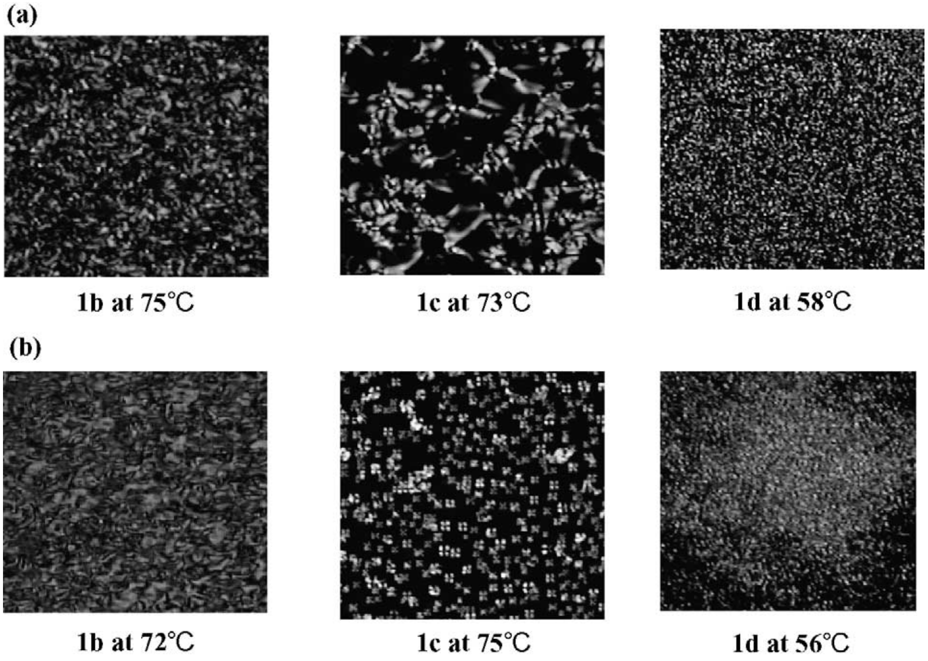


Fig. 1. Optical textures of nematic phases of **1b–1d** on cooling (a) and on heating (b); magnification 200×.

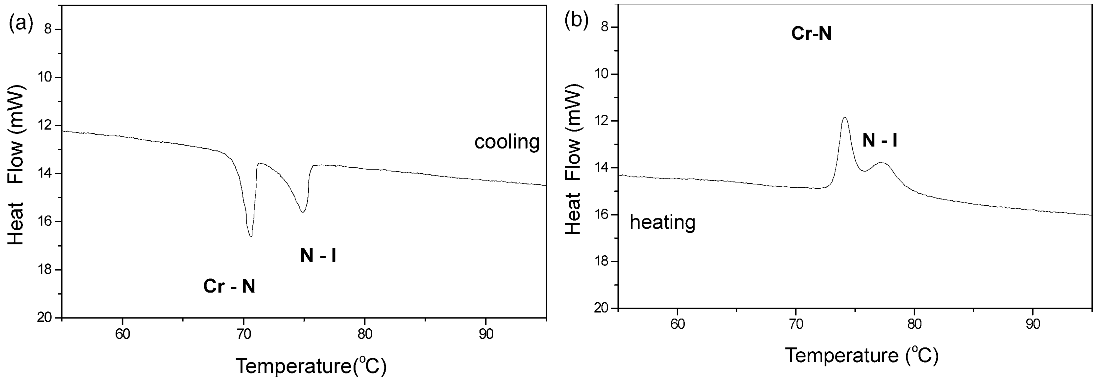


Fig. 2. DSC thermograms of **1b** on cooling (a) and heating (b).

rubbing with the same cell gap. The TN cell showed the white state at 72 °C without voltage, but showed the black state at the same temperature with 15 V voltage. It can be understood a nematic phase at 72 °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 and the phases for **1a–1d** (*n* = 6–9) are shown in Table 1. For the comparison, phase transition temperatures of other LC materials (**2–4**) are included.

Generally speaking, 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

Table 1
Transition temperatures of spirobenzopyranylated LC molecules on cooling from isotropic liquid

Compd	Cr		SmC		SmA		N		I	Notes
1a	•		–		–		–	77.5	•	This work
1b	•	70.5	–		–		•	74.9	•	This work
1c	•	63.6	–		–		•	74.5	•	This work
1d	•	53.5	–		–		•	57.5	•	This work
2 ($n=7$)	•	129	•	198	•	203	•	228	•	Ref. [10]
3 ($n=7$)	•	113	–		•	187	•	224	•	Ref. [12]
4 ($n=7$)	•	60	–		–		•	98.7	•	Ref. [12]

rest of the structure. Traditionally, linking groups are used to extend the length and polarisability 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 our previous results, we found that the liquid crystal phase stability decrease in order of Series **2**–Series **3**–Series **4**–Series **1**, among the liquid crystallines containing a indolinobenzospiropyranyl group. Series **1**–Series **4** are identical except their connecting group. The fine structural differences of the two compounds results in entirely different LC phases. Series **1** and **4** have a flexible bond (–S–) between a spiropyranyl group and a mesogenic group, whereas Series **2** and **3** have planar moieties such as >C=O or –N=N–. This planar moieties may enhence polarisability anisotropy of the molecular core, and hence enhance the liquid crystal phase stability. This result implies that the flexible thio-linkage in this LC system does not enhence the liquid crystal phase stability. A sulfonyl group (–SOO–) is thus expected to enhance the LC stability.

Acknowledgements

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