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Synthesis and mesomorpic properties of liquid crystallines, alkyloxybenzoyloxy phenylated indolinobenzospiropyrans. Part 7[☆]

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Abstract

A thorough series of liquid crystalline compounds, alkoxybenzoyloxy-phenylated indolinobenzospiropyrans, **ABOP-SP 1a**–**1h** has been synthesized. These liquid crystal molecules have been synthesized via DCC esterification of 6-(4-hydroxyphenyl)-1′3′3′-trimethylspiro[2H-1-benzopyran-2,2-indoline] and 4-alkoxybenzoic acids. 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. Most of the compounds in the series that were examined exhibit monotropic nematic phases at the temperature range 89–103 °C on cooling from isotropic liquid. Among them, **ABOP-SP 1c** and **1e** are shown to exhibit a monotropic SmA phase, in addition to a nematic phase.

Keywords: Thermo and photochromic dyes; Indolinobenzospiropyrans; Liquid crystals; Monotropic SmA phase; Nematic phase

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1. Introduction

Photochromic spiropyran dyes have attracted wide attention for many applications in optical switching, high-density optical data storage, holographic systems and optical computing [2,3]. Most studies have focused on derivatives having an electron-withdrawing group such as an NO_2 group substituted to the 6-position of the spiropyran to utilize the photochemical ring opening reaction due to its stabilized merocyanine form. Recently, however, our group has been studying the so-called non-activated spiropyrans [4–6] which lack a strong electron withdrawing substituent, and are also useful in many respects. A few examples of spiropyran-containing mesogens have also been reported. Krongauz and co-workers proposed a quasi-liquid crystal phase with physial properties analogous to that of a nematic phase [7,8]. Other groups also reported works which incorporated a spiropyran unit as a photochromic or thermochromic side-chain in polymeric nematic liquid crystals and cyclic siloxanes [9,10]. These LC materials show considerable potential as candidates for photoresolvable dopants in UV-trans-

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parent 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. Spiropyran (SP) is inherently a chiral compound that undergoes a reversible photochemical ring opening to give achiral merocyanine (MC). When irradiated with unpolarized light, the prochiral MC undergoes ring closure to form (R)-SP or (S)-SP at equal rates and under such conditions of the photostationary state, the SP exists as rapidly interconverting enantiomers [11–13]. In order to induce a 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. Because this light-induced interconversion can be sensed by the change in the optical rotatory power of the liquid crystal, it may serve as the basis for the liquid crystal optical switch [14–16].

For the development of a ferroelectric liquid crystal optical switch, we have thus recently expanded our research into smectic C (SmC) mesogens incorporating a non-activated spiropyran unit. None of the smectic phases have been detected from series **1** (*n* = 4, 6–8), unlikely in series of **2** [11,12,17]. Recently, however, a SmA phase was detected in the case of **1c** (*n* = 3), which encourage us to reinvestigate series **1**, thoroughly. In this report we describe the synthesis and characterization of a thorough series of liquid crystalline compounds containing a non-activated Indolinobenzospiropyran, **ABOP-SP 1a–1h**.

2. Experimental

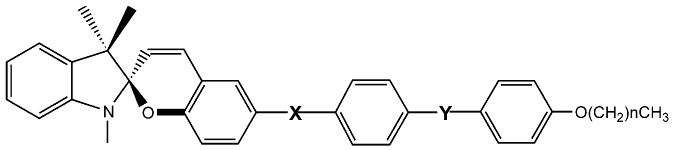
2.1. General

Melting points were determined using a Fischer–Jones melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained in deuterated chloroform on a Varian 300 NMR spectrophotometer. Chemical shifts were reported in δ (ppm) relative to tetramethylsilane as the internal standard. High-resoution FAB mass spectra were obtained by the Basic Science Research Institute. The DSC thermograms of the compounds were obtained using a DuPont 910 Thermal Analyzer calibrated with indium under a 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 micron cell with planar alignment were made by the general method using a commercial align-material, 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 dis-



1: X = - , Y = OCO (**1a**, n=0; **1b**, n=2; **1c**, n=3; **1e**, n=5) This work
(**1d**, n=4; **1f**, n=6; **1g**, n=7; **1h**, n=8) Earlier work
2: X = OCO, Y = - (**2a**, n=6; **2b**, n=7; **2c**, n=8) Earlier work

tilled from calcium hydride prior to use. 5-(4-Hydroxyphenyl) salicylaldehyde **3** was prepared by formylation of 4,4′-biphenol via the Reimer–Tiemann reaction. 6-(4-Hydroxyphenyl)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] **4** was prepared by condensation of 2-methylene-1,3,3-trimethylindoline (**2**, Fischer base) with 5-(4-hydroxyphenyl)salicylaldehyde **3**, using the usual procedure [4]. The 4-alkoxybenzoic acids **6** were prepared from oxidation of 4-hydroxy aldehyde **5** using $KMnO_4$ in acetone, followed by alkylation with the corresponding alkyliodides in K_2CO_3/acetonitile.

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

The following procedure is representative. To a solution of 6-(4-hydroxyphenyl)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] **4** (0.14 nmol), and 4-alkoxybenzoic acids, **6** (0.14 mmol) in 30 ml of dried CH_2Cl_2 was added 1,3-dicyclohexyl-carbodiimide (DCC, 0.56 mmol) and 4-dimethylaminopyridine (DMAP, 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 (15:1 hexane/ethyl acetate) which gave 0.14 g of orange solid, **1**. The product was further purified by recrystallization from acetone to give a white solid.

2.3.1. *1′,3′,3′-Trimethyl-6-[4-(4-methyloxybenzoyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline]* ***(1a)***

Yield 83%. M.p. 193 °C. ^{1}H NMR δ 7.12 (d, *J* = 7.1 Hz), 6.79 (m, 1H), 7.14 (m, 1H), 6.58 (d, *J* = 7.6 Hz), 1.12 (s, 3H), 1.25 (s, 3H), 2.78 (s, 3H), 3.88 (s, 3H), 5.84 (d, *J* = 10.2 Hz), 7.11 (d, *J* = 10.2 Hz), 7.56 (s, 1H), 7.44 (d, *J* = 8.4 Hz), 6.78 (d, *J* = 8.4 Hz), 7.68 (d, *J* = 8.6 Hz), 7.31 (d, *J* = 8.6 Hz), 8.11 (d, *J* = 8.8 Hz), 7.14 (d, *J* = 8.8 Hz). M.w 503.21, Molecular ion 503 (*m*/*z*), 56% (rel. intensity), High-resolution MS: calculated 503.2097 for $C_{33}H_{29}NO_4$; found; 503.2092. Anal. calcd: C, 78.71; H, 5.80; N, 2.78; Found: C, 78.9; H, 5.84; N, 2.80.

2.3.2. *1′,3′,3′-Trimethyl-6-[4-(4-propyloxybenzoyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline]* ***(1b)***

Yield 92%. M.p. 181 °C. ^{1}H NMR δ 7.10 (d, *J* = 7.2 Hz), 6.86 (m, 1H), 7.19 (m, 1H), 6.55 (d, *J* = 7.7 Hz), 1.07 (t, 3H), 1.19 (s, 3H), 1.34 (s, 3H), 1.87(m, 2H), 2.76 (s, 3H), 4.02 (t, 2H), 5.74 (d, *J* = 10.2 Hz), 6.93 (d, *J* = 10.2 Hz), 7.27 (s, 1H), 7.33 (d, *J* = 8.4 Hz), 6.78 (d, *J* = 8.4 Hz), 7.57 (d, *J* = 8.6 Hz), 7.24 (d, *J* = 8.6 Hz), 8.16 (d, *J* = 8.8 Hz), 6.99 (d, *J* = 8.8 Hz). M.w 531.24, Molecular ion 531 (*m*/*z*), 93% (rel. intensity), High-resolution MS: calculated 531.2410 for $C_{35}H_{33}NO_4$; found; 531.2427. Anal. calcd: C, 79.07; H, 6.26; N, 2.63; Found: C, 79.14; H, 6.25; N, 2.65.

2.3.3. *1′,3′,3′-Trimethyl-6-[4-(4-butyloxybenzoyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline]* ***(1c)***

Yield 95%. M.p. 186 °C. ^{1}H NMR δ 7.08 (d, *J* = 7.2 Hz), 6.85 (m, 1H), 7.18 (m, 1H), 6.54 (d, *J* = 7.6 Hz), 1.00 (t, 3H), 1.18 (s, 3H), 1.34 (s, 3H), 1.87 (m, 2H), 2.76 (s, 3H), 4.04 (t, 2H), 5.72 (d, *J* = 10.3 Hz), 6.92 (d, *J* = 10.2 Hz), 7.25 (s, 1H), 7.32 (d, *J* = 8.4 Hz), 6.78 (d, *J* = 8.4 Hz), 7.55 (d, *J* = 8.3 Hz), 7.23 (d, *J* = 8.3 Hz), 8.15 (d, *J* = 8.5 Hz), 6.97 (d, *J* = 8.5 Hz). M.w 545.26, Molecular ion 545 (*m*/*z*), 100% (rel. intensity), High-resolution MS: calculated 545.2566 for $C_{36}H_{35}NO_4$; found; 545.2578. Anal. calcd: C, 79.24; H, 6.47; N, 2.57; Found: C, 79.0; H, 6.48; N, 2.56.

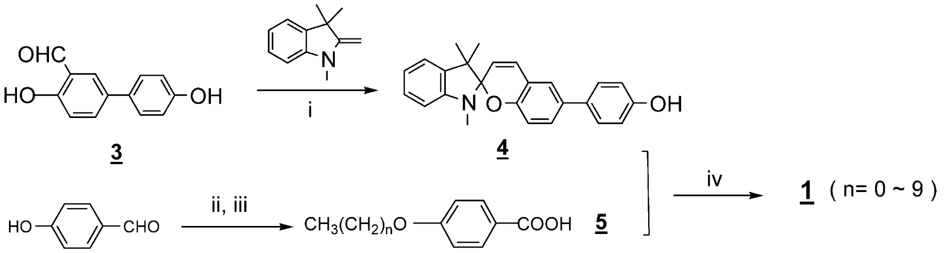
2.3.4. *1′,3′,3′-Trimethyl-6-[4-(4-hexyloxybenzoyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline]* ***(1e)***

Yield 90%. M.p. 179 °C. ^{1}H NMR δ 7.09 (d, *J* = 7.3 Hz), 6.85 (m, 1H), 7.18 (m, 1H), 6.54 (d, *J* = 7.7 Hz), 0.92 (t, 3H), 1.19 (s, 3H), 1.29–1.48 (m, 9H), 1.82 (m, 2H), 2.76 (s, 3H), 4.04 (t, 2H), 5.74 (d, *J* = 10.2 Hz), 6.92 (d, *J* = 10.2 Hz), 7.26 (s, 1H), 7.32 (d, *J* = 8.4 Hz), 6.79 (d, *J* = 8.4 Hz), 7.55 (d, *J* = 8.5 Hz), 7.23 (d, *J* = 8.5 Hz), 8.15 (d, *J* = 8.7 Hz), 6.98 (*d*, *J* = 8.7 Hz). M.w 573.73, Molecular ion 574 (*m*/*z*), 100% (rel. intensity), High-resolution MS: calculated 573.2879 for $C_{38}H_{39}NO_4$; found; 573.2892. Anal. calcd: C, 79.55; H, 6.85; N, 2.44; Found: C, 79.60; H, 6.86; N, 2.45.

3. Results and discussion

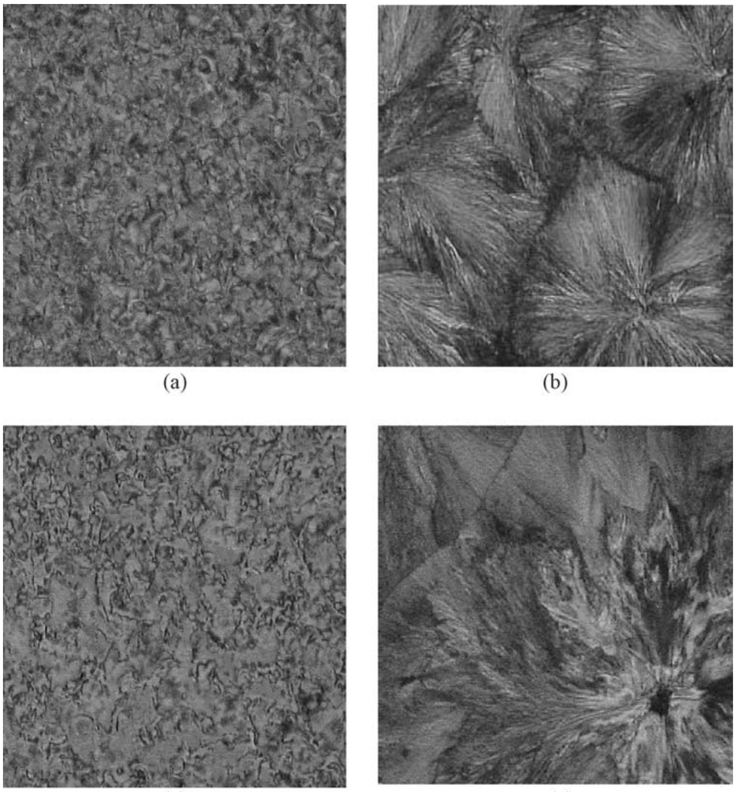
3.1. Synthesis

The present compounds were synthesized by general DCC esterification of 6-(4-hydroxyphenyl)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] **4** with the corresponding 4-alkoxybenzoic acids, **5** shown in Scheme 1. The final compounds obtained by column chromatography were recrystallized again from ethyl acetate. Their purity and structure were confirmed by



i : DMF, heat, ii : K_2CO_3, RI / CH_3CN
iii: $MgSO_4$, $KMnO_4$ / acetone, iv : DCC, DMAP

Scheme 1.



(c) (c)

Fig. 1. Optical photomicrographs of **1c** on cooling from isotropic liquid: (a) nematic phase at 103 °C, (b) SmA phase at 68 °C and **1e**: (c) nematic phase at 102 °C, (d) SmA phase at 88 °C; magnification 200×.

^{1}H NMR spectroscopy, as described in Section 2.1.

3.2. Mesophase characterization

The characterization of liquid crystal phases exhibited by spiropyran moieties were studied by differential scanning calorimetry (DSC), optical polarizing microscopy, and the electro-optical method. Most of the compounds studied exhibited mesomorphic behavior on the first cooling and the subsequent heating cycle. Because of the thermo- and photochromic properties of the spiropyran dyes, the amount of the ring-opened merocyanine species may not be negligible at high temperature [17]. However, it is supposed that the presence of mesophase in the first cooling stage was shown by reorientation of the spiropyran molecules in the isotropic liquid. The amount of ring-opened merocyanine is negligible in the solid state.

In series **1**, all the compounds formed monotropic nematic phases. Both **1c** and **1e** formed an additional smectic phase. As a result of the polarizing microscopy study for **1c** and **1e** showed a nematic and SmA on cooling from the istropic phase, as shown in Fig. 1 [18–20].

From the DSC thermogram obtained from **1c** (Fig. 2), the first and second weak peaks at 103 and 70 °C on cooling were identified to be a nematic and a SmA phase, respectively. Upon lowering the temperature further, the next transition below corresponding to the appearance of the SmC phase, was not revealed.

Phase transition temperatures of 1′,3′,3′-trimethyl-6-[4-(4-butyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline] (**ABOP-SP**, **1a**–**1h**) are summarized in Table 1.

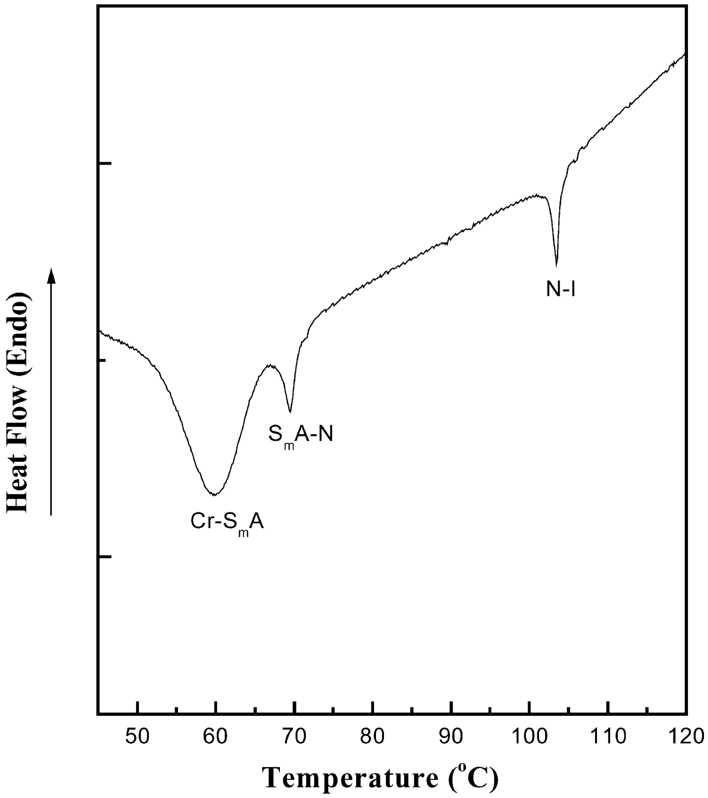


Fig. 2. A DSC thermogram of **ABOP-SP** (**1c**) on cooling from isotropic liquid.

In order to confirm further the phases obtained by thermal fluctuation from DSC and by texture from optical microscopy for **ABOP-SP 1a–1h**, we used a normal twisted nematic (TN) cell with a 4.5 μm cell gap and a 4 μm cell with planar alignment applied one side rubbing with the same cell gap. The TN cell showed the white state at 110 °C without voltage, but showed the black state at the same temperature with 15 V voltage. This shows a nematic phase at 110 °C. In the case of the 4 μm cell with planar alignment at 80 °C, there was no change of transmittance even though we applied the electric field in the range 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 80 °C without applying the electric field under the two crossed polarizers, the highest transmittance (white state) was from rotating at a 45° angle from the black state. From these results, we confirmed this compound (**1c** and **1e**) has a nematic and a SmA phase. A TGA thermogram showed **1c** has a different weight loss pattern from others such as **1f** and **1h** as shown in Fig. 3.

Unfortunately, at present we do not understand the reason for the uniqueness of **1c**. We can only suggest that it could be related to the unique crystal structures, which are yet to be determined, as shown in a TGA thermogram. In comparison, LC molecules, **2a**–**2c** formed nematic and SmA phases on cooling and especially, **2b** showed a second-order phase transition at 71 °C corresponding to a SmC phase, as reported earlier [12]. Further work to understand the uniqueness of **1c** and **1e**, and to develop photoresolvable spiropyran-containing SmC mesogens is in progress.

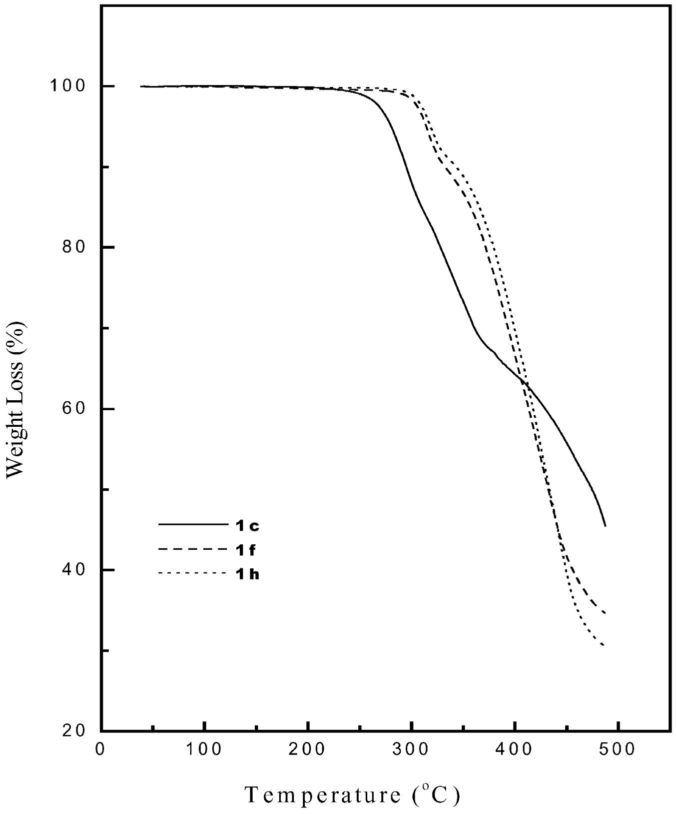


Fig. 3. TGA thermograms of **ABOP-SP** (**1c**, **1f** and **1h**).

Table 1
Phase transition temperature of 1′,3′,3′-trimethyl-6-[4-(4-butyloxy)-phenyl]spiro[2H-1-benzopyran-2,2′-indoline] (**ABOP-SP**, **1a**–**1h**) on cooling from isotropic liquid

	Cr		SmC		SmA		N		I	Note
1a ($n=0$)	•	61	–		–		•	91	•	[a]
1b ($n=2$)	•	58	–		–		•	92	•	[a]
1c ($n=3$)	•	60	–		•	70	•	103	•	[a]
1d ($n=4$)	•	72	–		–		•	102	•	[b]
1e ($n=5$)	•	80	–		•	90	•	102	•	[a]
1f ($n=6$)	•	69	–		–		•	97	•	[b]
1g ($n=7$)	•	76	–		–		•	91	•	[b]
1h ($n=8$)	•	65	–		–		•	89	•	[b]
2a ($n=6$)	•	78	–		•	104	•	107	•	[b]
2b ($n=7$)	•	60	•	71	•	99	•	103	•	[b]
2c ($n=8$)	•	72	–		•	90	•	89	•	[b]

[a] This work.
[b] Ref. [12].

Acknowledgements

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