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Synthesis and properties of new liquid crystalline compounds containing an indolinobenzospiropyranylazo group. Part 3☆

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Abstract

Two series of liquid crystalline dyes (series **1** and **2**) containing novel mesogens incorporating a non-activated spiropyranylazo group have been synthesized. Those mesogens are derived from [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azobenzoic acid and 6-(*p*-hydroxyphenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] for the series **1** and **2**, respectively. Their liquid crystalline properties were studied by differential scanning calorimetry, optical polarizing microscopy and electro-optical measurement. Most of the compounds in series **1** form the enantiotropic nematic phase, while compounds in series **2** form the monotropic nematic and SmA phase.

Keywords: Non-activated spiropyran; Arylazoindolinobenzospiropyran dye; Chiral dopant; Nematic and smectic A phase; Liquid crystal optical switch

1. Introduction

Organic photochromic compounds, which can be reversibly written to and read from by light, are obvious potential for the light-controlled devices. Development of these materials requires discovery of compounds that exhibit two distinct chemical or physical forms that are interconverted and detected by light without their destruction. Photochromic spiropyran dyes have thus attracted wide attention for potential application in optical switching, high-density optical data storage and optical computing [1–3].

So far, studies have focused on derivatives having an electron-withdrawing group such as $-NO_2$ group substituted in the 6-position of the spiropyran so as to utilize the photochemical ring opening reaction of the stabilizing coloured merocyanine form, whereas much less attention has been paid to non-activated spiropyran derivatives which lack a strong electron withdrawing substituent [4–7].

Recently, we have begun to examine some of non-activated spiropyran dye systems [8–11]. During studies on non-activated spiropyran dye systems, we found that the 4′-octyloxybiphenyl-4-carboxylate derivatives exhibited a monotropic

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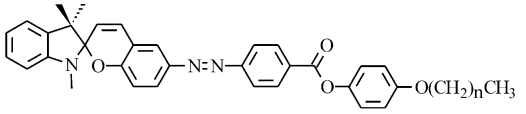
Sm*C phase [9]. This was the first case of a spiropyran containing a SmC mesogen. These species hold considerable potential as candidates for photoresolvable dopants in UV-transparent nematic and polymeric nematic liquid crystal phases.

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 [12]. In order to induce a nematic–cholesteric phase transition via the photoresolution of spiropyran (SP) dopant, it is important that the photostationary state concentration of the SP- merocyanine (MC) pair favours the SP component. Because this light-induced interconversion can be detected by the change in optical rotatory power of the liquid crystal, it may serve as the basis for a liquid crystal optical switch [13–15].

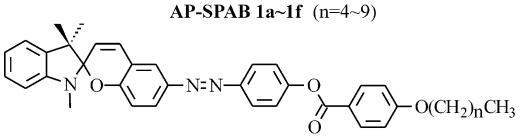
Our research have focused on non-activated SP molecules which possess the chiroptical properties essential for a liquid crystal optical switch (LCOS) based on the photoresolution. We have thus expanded our research into smectic C (SmC) mesogens that incorporate a non-activated spiropyran unit. In a previous paper [10], the SmC character was detected from the LC dyes incorporating a non-activated spiropyran unit whose structure is shown below:

SP–N=N–Ph–COO–Ph–Ph–OR R:–C_7H_{15} and –C_9H_{19}

In this paper, we describe the synthesis and properties of the series **1, AP-SPAB** and **2, SPAP-APC**.



AP-SPAB 1a~1f (n=4~9)



SPAP-APC 2a~2f (n=4~9)

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 deuterated chloroform on a Varian 300 NMR spectrophotometer; chemical shifts were reported in δ (ppm) relative to tetramethylsilane as internal standard. IR spectra were taken with an Shimadzu FT-IR 8501 using KBr pellets. Electron Impact (EI) mass spectra were recorded on a Schimadzu GCMS-QP1000 spectrophotometer. The DSC thermograms of the compounds were obtained on a DuPont 910 Thermal Analyzer calibrated with indium under N_2 atmosphere at a heating/cooling rate of 7 °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 ferroelectric cell (F-cell) were made by 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 F-cell, respectively, and our compound filled slowly at the temperature of isotropic phase. The thickness of cell gap was controlled uniformly using a 4.5 μm spacer for electro-optical study.

2.2. Materials

All reagent were purchased from the commercial sources and were used without further purification unless otherwise noted. Fischer's base, various alkyl halides, 1,3-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich. Methylene chloride (CH_2Cl_2) was distilled from calcium hydride prior to use. *N,N*-dimethylformamide (DMF) was distilled using Linde type 4A molecular sieves.

2.3. Synthesis

2.3.1. Synthesis of 4-(3′-formyl-4′-hydroxyphenylazo) benzoic acid (**3**)

A solution of $NaNO_2$ (1.6 g, 23.2 mmol) in H_2O (40 ml) was added to salicylaldehyde (2.8 g, 21.8

mmol) in aq. NaOH (1.8 g) keeping the temperature at 5 °C. The resulting solution was added dropwise to a solution of 4-aminobenzoic acid (3.2 g, 23.2 mmol) in aq. HCl (1.6 g) at 0 °C. Following addition, the reaction mixture was stirred for 1h at room temperature and the precipitate was filtered and washed three times with distilled water. Recrystallization from acetone afforded 4.2 g as red-brown solid in 69% yield; mp 270 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.18 (d, 1H), 7.90 (d, J = 8.1 Hz, 2H), 8.09 (d, 1H), 8.11 (d, J = 8.2 Hz, 2H), 8.19 (s, 1H).

2.3.2. Synthesis of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-p-benzoic acid (**4**)

Fischer's base (1.90 g, 21.6 mmol) was added to a solution 2′-hydroxybenzaldehyde-5′-yl azo-*p*-benzoic acid (3.8 g, 27.0 mmol) in 100 ml of DMF. The mixture was stirred for 5 h at room temperature. After reaction was complete, the mixture was poured into 200 ml of distilled water and extracted with ethyl acetate (3×200 ml). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. Recrystallization from ethyl acetate/hexane gave 6.8 g as light-red crystal in yield 73%; mp 228 °C; IR (cm^{-1}) 3430 (m), 2959 (m), 2668 (w), 2534 (w), 1688 (s), 1603 (s), 1484 (s), 1262 (s), 955 (m), 741 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (s, 3H), 1.31 (s, 3H), 2.75 (s, 3H), 5.88 (d, J = 10.2 Hz, 1H), 6.54 (d, 1H), 6.83 (d, 1H), 6.85 (t, 1H), 6.96 (d, J = 10.2 Hz, 1H), 7.08 (d, J = 7.21 Hz, 1H), 7.19 (t, 1H), 7.72 (s, 1H), 7.77 (d, J = 8.80 Hz, 1H), 7.90 (d, J = 8.60 Hz, 2H), 8.22 (d, J = 8.60 Hz, 2H).

2.3.3. General procedure for the esterification of compound **4**: synthesis of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-(4′-hexyloxyphenyl)benzoate (**1b**)

Benzoates derivatives were synthesized from the reaction of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-*p*-benzoic acid (**4**) and with the corresponding 4-alkyloxyphenols. A representative reaction is following: 1,3-dicyclohexylcarbodiimide (DCC, 0.22 g, 1.12 mmol) and 4-dimethylaminopyridine (DMAP, 0.06 g, 0.44 mmol) were added to a solution of 4-hexyloxyphenol (0.20 g, 1.02 mmol) and solution of **4** (0.40 g, 0.94 mmol) in 80 ml of dried CH_2Cl_2. The mixture was stirred at room temperature and monitored by TLC until completion of the reaction. The solvent was removed in vacuo and the ester purified by column chromatography on silica gel (15:1 hexane/ethyl acetate) which gave 0.31 g of a permanent yellow coloured solid. The product was further purified by recrystallization from acetone: yield 73%; mp 137 °C; IR (cm^{-1}) 3355 (m), 2939 (s), 2854 (s), 1755 (s), 1621 (s), 1264 (s), 1208 (s), 1017 (m), 961 (s), 719 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H), 1.20 (s, 3H), 1.34 (s, 3H), 1.33–1.47 (m, 6H), 1.81 (m, 2H), 2.77 (s, 3H), 3.97 (t, 2H), 5.81 (d, J = 10.3 Hz, 1H), 6.56 (d, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.87 (t, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.98 (d, 1H), 7.10 (d, 1H), 7.14 (d, 2H), 7.20 (t, 1H), 7.75 (s, 1H), 7.81 (d, 1H), 7.95 (d, J = 8.4 Hz, 2H), 8.32 (d, 2H).

2.3.4. Synthesis of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-(4′-pentyloxyphenyl)benzoate (**1a**)

Yield 68%; mp 131 °C; IR (cm^{-1}) 3355 (m), 2930 (s), 2850 (s), 1734 (s), 1625 (s), 1265 (s), 1207 (s), 1022 (m), 963 (s), 723 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H), 1.21 (s, 3H), 1.34 (s, 3H), 1.33–1.51 (m, 4H), 1.81 (m, 2H), 2.78 (s, 3H), 3.98 (t, 2H), 5.82 (d, J = 10.2 Hz, 1H), 6.57 (d, 1H), 6.86 (d, J = 8.7 Hz, 1H), 6.88 (t, 1H), 6.94 (d, J = 9.2 Hz, 2H), 6.99 (d, 1H), 7.09 (d, 1H), 7.15 (d, 2H), 7.21 (t, 1H), 7.75 (s, 1H), 7.82 (d, 1H), 7.95 (d, J = 8.6 Hz, 2H), 8.32 (d, 2H).

2.3.5. Synthesis of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-(4′-heptyloxyphenyl)benzoate (**1c**)

Yield 79%; mp 125 °C; IR (cm^{-1}) 3358 (m), 2930 (s), 2851 (s), 1735 (s), 1633 (s), 1273 (s), 1210 (s), 1022 (m), 961 (s), 722 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H), 1.20 (s, 3H), 1.34 (s, 3H), 1.29–1.49 (m, 8H), 1.81 (m, 2H), 2.77 (s, 3H), 3.99 (t, 2H), 5.82 (d, J = 10.2 Hz, 1H), 6.56 (d, 1H), 6.86 (d, J = 8.7 Hz, 1H), 6.88 (t, 1H), 6.94 (d, J = 8.7 Hz, 2H), 6.97 (d, 1H), 7.10 (d, 1H), 7.15 (d, 2H), 7.21 (t, 1H), 7.75 (s, 1H), 7.83 (d, 1H), 7.95 (d, J = 8.4 Hz, 2H), 8.33 (d, 2H).

*2.3.6. Synthesis of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-(4′-octyloxyphenyl)benzoate (**1d**)*

Yield 84%; mp 103 °C; IR (cm^{-1}) 3351 (m), 2945 (s), 2864 (s), 1766 (s), 1637 (s), 1268 (s), 1207 (s), 1022 (m), 960 (s), 723 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.20 (s, 3H), 1.34 (s, 3H), 1.30–1.48 (m, 10H), 1.79 (m, 2H), 2.78 (s, 3H), 3.97 (t, 2H), 5.82 (d, $J=10.2$ Hz, 1H), 6.56 (d, 1H), 6.86 (d, $J=8.7$ Hz, 1H), 6.87 (t, 1H), 6.94 (d, $J=9.0$ Hz, 2H), 6.97 (d, 1H), 7.10 (d, 1H), 7.14 (d, 2H), 7.20 (t, 1H), 7.74 (s, 1H), 7.81 (d, 1H), 7.95 (d, $J=8.4$ Hz, 2H), 8.32 (d, 2H).

*2.3.7. Synthesis of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-(4′-nonyloxyphenyl)benzoate (**1e**)*

Yield 72%; mp 108 °C; IR (cm^{-1}) 3355 (m), 2933 (s), 2851 (s), 1734 (s), 1624 (s), 1267 (s), 1208 (s), 1020 (m), 961 (s), 723 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H), 1.20 (s, 3H), 1.34 (s, 3H), 1.31–1.48 (m, 12H), 1.80 (m, 2H), 2.78 (s, 3H), 3.99 (t, 2H), 5.82 (d, $J=10.5$ Hz, 1H), 6.58 (d, 1H), 6.86 (d, $J=8.6$ Hz, 1H), 6.87 (t, 1H), 6.94 (d, $J=9.0$ Hz, 2H), 6.97 (d, 1H), 7.10 (d, 1H), 7.15 (d, 2H), 7.21 (t, 1H), 7.75 (s, 1H), 7.83 (d, 1H), 7.95 (d, $J=8.6$ Hz, 2H), 8.33 (d, 2H).

*2.3.8. Synthesis of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-(4′-decyloxyphenyl)benzoate (**1f**)*

Yield 80%; mp 84 °C; IR (cm^{-1}) 3350 (m), 2935 (s), 2849 (s), 1717 (s), 1636 (s), 1255 (s), 1212 (s), 1018 (m), 963 (s), 723 (m); ^1H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H), 1.20 (s, 3H), 1.34 (s, 3H), 1.29–1.49 (m, 14H), 1.81 (m, 2H), 2.78 (s, 3H), 3.97 (t, 2H), 5.82 (d, $J=10.2$ Hz, 1H), 6.58 (d, 1H), 6.86 (d, $J=8.7$ Hz, 1H), 6.89 (t, 1H), 6.95 (d, $J=9.0$ Hz, 2H), 6.99 (d, 1H), 7.10 (d, 1H), 7.14 (d, 2H), 7.21 (t, 1H), 7.74 (s, 1H), 7.82 (d, 1H), 7.95 (d, $J=8.4$ Hz, 2H), 8.32 (d, 2H).

*2.3.9. Synthesis of 6-(*p*-hydroxyphenylazo)-1′,3′4,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**6**)*

p-Aminophenol was reacted with *p*-toluenesulfonylchloride in the presence of triethylamine [13]. The recrystallized white grey solid, 4-(*p*-toluenesulfonyloxy)aniline in aq. HCl, was reacted with a solution of $NaNO_2$ in H_2O at 0 °C. The resulting cold solution was added slowly to salicylaldehyde in 20% aq. NaOH and the mixture kept at 0 °C for further 2 h. The prepared orange solid, 6-(*p*-toluenesulfonyloxyphenylazo)-salicylaldehyde **5** was obtained. The compound **5** reacted with Fischer's base in DMF to form 6-(*p*-toluenesulfonyloxyphenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline]. The solution of 6-(*p*-toluenesulfonyloxyphenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (2.0 g, 3.43 mmol) in ethanol (80 ml) was added a solution KOH (0.29g, 5.14mmol) in H_2O (10 ml) and refluxed for 8 h. The reaction mixture was evaporated to dryness and purified by column chromatography on silica gel (20:1 hexane/ethyl acetate) which gave 1.01 g of dark-green solid **6** in yield 68%; mp 88 °C; IR (cm^{-1}) 3407 (w), 2964 (w), 1618 (m), 1475 (s), 1249 (m), 960 (w), 821 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 3H), 1.32 (s, 3H), 2.76 (s, 3H), 5.78 (d, $J=10.2$ Hz, 1H), 6.55 (d, $J=7.5$ Hz, 1H), 6.82 (d, $J=8.7$ Hz, 1H), 6.86 (t, 1H), 6.93 (d, $J=8.4$ Hz, 2H), 6.96 (d, 1H), 7.09 (d, 1H), 7.19 (t, 1H), 7.64 (s, 1H), 7.71 (d, 1H), 7.82 (d, 2H).

2.3.10. Synthesis of 4-alkoxybenzoic acid (7)

4-Alkoxybenzaldehyde, which was formed from the reaction of 4-hydroxybenzaldehyde with iodoalkane in the presence of potassium carbonate, was oxidized with $KMnO_4$ in acetone. The following procedure is representative; 4-Hexyloxybenzaldehyde (3.69 g, 17.9 mmol), $MgSO_4$ (2.16 g, 17.9 mmol) and $KMnO_4$ (3.39 g, 21.5 mmom) in acetone (150 ml) was stirred for 5 h. The resulting solution was poured into 2 N HCl (150 ml) and saturated with NaCl. The product was extracted into ethyl acetate, dried with $MgSO_4$ and evaporated to dryness. The crude product was recrystallized from acetone/hexane to give 2.90 g (96% yield) as; mp 90 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, 3H), 1.13–1.41 (m, 6H), 1.71 (q, 2H), 4.05 (t, 2H), 7.02 (d, $J=8.4$ Hz, 2H), 7.93 (d, 2H), 12.61 (s, 1H).

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

The desired compound was prepared according to the same method as the procedure for the

esterification of **4**. The crude product was purified by column chromatography on silica gel (20:1 hexane/ethyl acetate) and the product were further purified by recrystallization from acetone or ethyl acetate.

*2.4.1. Synthesis of [6-(1″-phenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2-2′-indoline]-4″-yl-(4-pentyloxyphenyl)carboxylate (**2a**)*

Yield 87%; mp 169 °C; IR (cm^{-1}) 3354 (m), 2958 (w), 1729 (s), 1607 (s), 1485 (s), 1259 (s), 1167 (s), 1070 (m), 960 (m), 815 (w), 743 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 0.95 (t, 3H), 1.20 (s, 3H), 1.33 (s, 3H), 1.38–1.49 (m, 4H), 1.84 (m, 2H), 2.77 (s, 3H), 4.05 (t, 2H), 5.79 (d, $J=10.2$, 1H), 6.56 (d, $J=7.5$ Hz, 1H), 6.84 (d, $J=9.0$ Hz, 1H), 6.87 (t, 1H), 6.98 (d, 1H), 6.99 (d, $J=8.7$ Hz, 2H), 7.10 (d, 1H), 7.20 (t, 1H), 7.34 (d, $J=9.0$ Hz, 2H), 7.69 (s, 1H), 7.75 (d, 1H), 7.94 (d, 2H), 8.16 (d, 2H).

*2.4.2. Synthesis of [6-(1″-phenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2-2′-indoline]-4″-yl-(4-hexyloxyphenyl)carboxylate (**2b**)*

Yield 78%; mp 156 °C; IR (cm^{-1}) 3349 (m), 2955 (m), 1727 (s), 1607 (s), 1485 (s), 1259 (s), 1171 (s), 1073 (s), 963 (s), 812 (w), 744 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H), 1.20 (s, 3H), 1.33 (s, 3H), 1.31–1.49 (m, 6H), 1.82 (m, 2H), 2.77 (s, 3H), 4.05 (t, 2H), 5.79 (d, $J=10.5$, 1H), 6.57 (d, $J=7.7$ Hz, 1H), 6.85 (d, $J=8.8$ Hz, 1H), 6.89 (t, 1H), 6.97 (d, 1H), 6.99 (d, $J=8.8$ Hz, 2H), 7.11 (d, 1H), 7.20 (t, 1H), 7.34 (d, $J=8.9$ Hz, 2H), 7.70 (s, 1H), 7.76 (d, 1H), 7.95 (d, 2H), 8.15 (d, 2H).

*2.4.3. Synthesis of [6-(1″-phenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2-2′-indoline]-4″-yl-(4-heptyloxyphenyl)carboxylate (**2c**)*

Yield 80%; mp 148 °C; IR (cm^{-1}) 3355 (m), 2927 (m), 1731 (s), 1607 (s), 1486 (s), 1258 (s), 1166 (s), 1071 (m), 959 (m), 814 (w), 744 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.20 (s, 3H), 1.34 (s, 3H), 1.32–1.47 (m, 8H), 1.81 (m, 2H), 2.77 (s, 3H), 4.05 (t, 2H), 5.79 (d, $J=10.3$, 1H), 6.57 (d, $J=7.5$ Hz, 1H), 6.84 (d, $J=9.0$ Hz, 1H), 6.87 (t, 1H), 6.97 (d, 1H), 6.99 (d, $J=8.7$ Hz, 2H), 7.10 (d, 1H), 7.20 (t, 1H), 7.35 (d, $J=8.9$ Hz, 2H), 7.71 (s, 1H), 7.75 (d, 1H), 7.95 (d, 2H), 8.16 (d, 2H).

*2.4.4. Synthesis of [6-(1″-phenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2-2′-indoline]-4″-yl-(4-octyloxyphenyl)carboxylate (**2d**)*

Yield 89%; mp 131 °C; IR (cm^{-1}) 3342 (m), 2927 (m), 1731 (s), 1607 (s), 1486 (s), 1258 (s), 1166 (s), 1071 (m), 959 (m), 814 (w), 744 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.20 (s, 3H), 1.33 (s, 3H), 1.38–1.49 (m, 10H), 1.82 (m, 2H), 2.77 (s, 3H), 4.05 (t, 2H), 5.79 (d, $J=10.5$, 1H), 6.56 (d, $J=7.6$ Hz, 1H), 6.84 (d, $J=8.9$ Hz, 1H), 6.87 (t, 1H), 6.97 (d, 1H), 6.98 (d, $J=9.0$ Hz, 2H), 7.09 (d, 1H), 7.20 (t, 1H), 7.34 (d, $J=9.0$ Hz, 2H), 7.69 (s, 1H), 7.76 (d, 1H), 7.94 (d, 2H), 8.16 (d, 2H).

*2.4.5. Synthesis of [6-(1″-phenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2-2′-indoline]-4″-yl-(4-nonyloxyphenyl)carboxylate (**2e**)*

Yield 87%; mp 130 °C; IR (cm^{-1}) 3350 (m), 2925 (s), 1730 (s), 1607 (s), 1486 (s), 1260 (s), 1166 (s), 1072 (m), 960 (m), 815 (w), 743 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H), 1.21 (s, 3H), 1.33 (s, 3H), 1.30–1.46 (m, 12H), 1.85 (m, 2H), 2.77 (s, 3H), 4.05 (t, 2H), 5.79 (d, $J=10.5$, 1H), 6.56 (d, $J=7.6$ Hz, 1H), 6.84 (d, $J=9.0$ Hz, 1H), 6.87 (t, 1H), 6.97 (d, 1H), 6.98 (d, $J=8.8$ Hz, 2H), 7.09 (d, 1H), 7.20 (t, 1H), 7.36 (d, $J=9.0$ Hz, 2H), 7.71 (s, 1H), 7.75 (d, 1H), 7.94 (d, 2H), 8.16 (d, 2H).

*2.4.6. Synthesis of [6-(1″-phenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2-2′-indoline]-4″-yl-(4-decyloxyphenyl)carboxylate (**2f**)*

Yield 72%; mp 121 °C; IR (cm^{-1}) 3349 (m), 2924 (s), 1728 (s), 1607 (s), 1487 (s), 1258 (s), 1165 (s), 1073 (m), 959 (m), 814 (w), 742 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, 3H), 1.20 (s, 3H), 1.34 (s, 3H), 1.35–1.48 (m, 14H), 1.84 (m, 2H), 2.77 (s, 3H), 4.05 (t, 2H), 5.78 (d, $J=10.5$, 1H), 6.56 (d, $J=7.8$ Hz, 1H), 6.85 (d, $J=8.8$ Hz, 1H), 6.87 (t, 1H), 6.97 (d, 1H), 6.99 (d, $J=8.8$ Hz, 2H), 7.09 (d, 1H), 7.20 (t, 1H), 7.35 (d, $J=9.0$ Hz, 2H), 7.71 (s, 1H), 7.76 (d, 1H), 7.94 (d, 2H), 8.17 (d, 2H).

3. Results and discussion

3.1. Synthesis

The spiropyranylazobenzoates **1a**–**1f** and the carboxylates **2a**–**2f** were synthesized by condensa-

tion of [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl] azo-benzoic acid (**4**) and 6-(*p*-hydroxyphenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**6**) with the corresponding 4-alkyloxyphenol and 4-alkyloxybenzoic acid, respectively, in the presence of dicyclohexylcarbodiimide (DCC) and 4-*N*,*N*-dimethylaminopyridine (DMAP). **4** and **6** were obtained from condensation reaction of Fischer's base with **3** and **5**, respectively. Those azo compounds, **3** and **5**, were prepared from the diazo coupling reaction of the corresponding amino compounds.

The synthetic routes for the LC compounds **1a**–**1f** and **2a–2f** were shown in Schemes 1 and 2, respectively. Characterization data of the synthesized liquid crystalline dyes are summarized in Table 1.

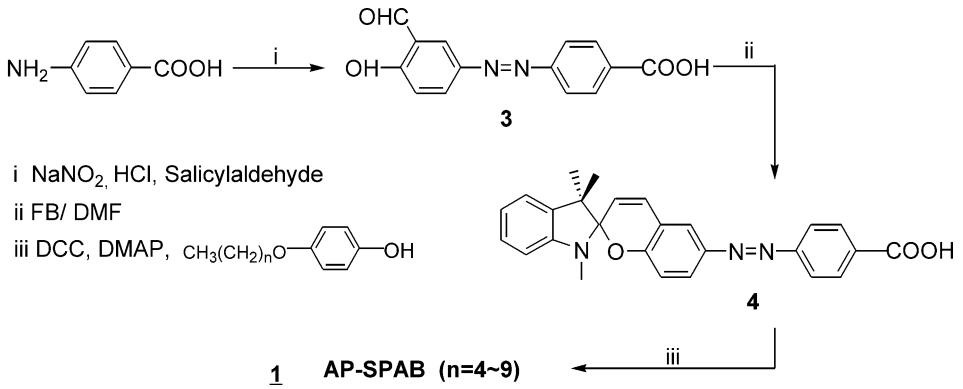
3.2. Spectroscopic properties of the LC compounds, *1a–1f* and *2a–2f*

The IR spectral frequencies of the synthesized spiropyran (SP), **1a**–**1f** and **2a**–**2f** were taken using KBr pellets, as described in the synthesis part. The azo frequencies of the SP was observed at 3340–3360 cm^{-1}. Aromatic ring C=C stretching absorption occurred at 1608–1616 cm^{-1}. The typical stretching vibration of the aryl C–O and C–N of the spiropyran derivatives was observed at 1257–1260 cm^{-1} and 1251–1282 cm^{-1}, respectively. The absorption peak of the ester group was observed at 1720–1732 cm^{-1} and the C_{spiro}–O stretching frequencies of the synthesized spiropyran occurred at 921–956 cm^{-1}. In the precursor **4**, aryl C–O stretching vibration absorption of the carboxylic acid was shown at 1255–1270 cm^{-1} and the absorption of the carbonyl group was detected at 1671–1700 cm^{-1}. Precursor 6 showed a broad absorption band of the OH group at 3410 cm^{-1} which overlapped with the absorption band of the azo group.

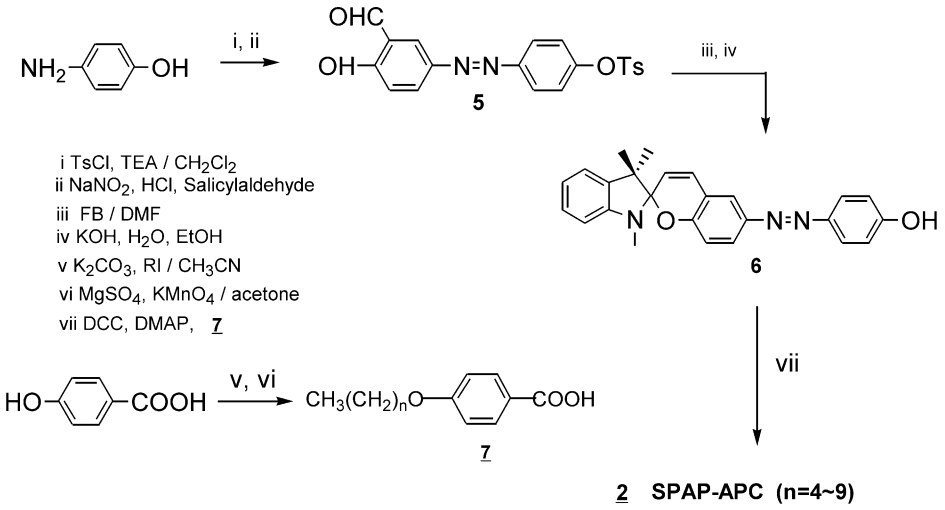
In therms of the proton NMR spectral data, the synthesized SP showed N–Me peaks at 2.62–2.77 ppm. The singlets of two geminal methyl groups occurred at 1.10–1.19 and 1.19–1.34 ppm for the 9-methyl and 8-methyl groups, respectively. In a previous *n*Oe experimental study of gem-dimethyl peaks of the spiropyran system, the methyl group C-9 was located close to the olefinic proton H3′ and the methyl group C-8 was located close to oxygen moiety of the pyranyl group [16]. The chemical shift of C-8 is expected to be in down field, compared to that of C-9, via a through-space interaction between the oxygen atom of pyran-ring and C-8 of indoline moiety. The olefinic protons appeared double-doublets at 5.68–5.84 and 6.94–7.02 ppm for H3′ and H4′, respectively. Their peaks have large coupling constants ($J = 10.2$–10.5 Hz) for both olefinic protons and hence those (H3′ and H4′) signals are very characteristic of the spiropyran system, as reported [16].

3.3. Mesophase characterization

The properties of the liquid crystal phases exhibited by the spiropyran moieties were studied



Scheme 1.



Scheme 2.

Table 1
Mps and other characterization data for the LC **1** and **2**

Compd.	mp (°C)	Color[a]	Yield (%)	M_w	Molecular ion	
					(*m*/*z*)	Rel. int. (%)
1a	138	P. yellow deep	68	587.72	588	100
1b	137	P. yellow deep	73	601.75	602	76
1c	125	P. yellow deep	79	615.77	616	100
1d	103	P. yellow deep	84	629.80	630	100
1e	108	P. yellow deep	72	643.83	644	100
1f	84	P. yellow deep	80	657.85	658	100
2a	169	orange	87	587.72	588	51
2b	156	P. yellow middle	78	601.75	602	100
2c	148	P. yellow middle	80	615.77	616	100
2d	131	P. yellow middle	89	629.80	630	76
2e	130	P. yellow middle	87	643.83	644	100
2f	124	P. yellow middle	72	657.85	658	100

[a] P. denotes "permanent".

using optical polarizing microscope equipped with a hot stage, differential scanning calorimeter and an electro-optical method. Although not all the compounds exhibited mesomorphic behavior on the first heating stage, they began to show a mesophase at the first cooling and subsequent heating-cooling stages. Because of the thermo- and photochromic properties of spiropyran dyes, the existence of a small portion of the ring-opened merocyanine species may not be negligible at high temperature [17]. However, it is presumed that the presence of a mesophase on the first cooling stage was demonstrated by reorientation of the spiropyran molecules in the isotropic liquid. The benzoates, **1a** and **1c** formed an enantiotropic nematic phase, while **1b** and **1d** formed a monotropic nematic phase with a typical Schlieren and marble texture as shown in Fig. 1(a) [18].

Fig. 2 shows DSC thermogram of **1a** from which the strong endothermic peak that corresponds to crystal–isotropic transition (Cr–I) at 135 °C was found on first heating. Two weak endothermic

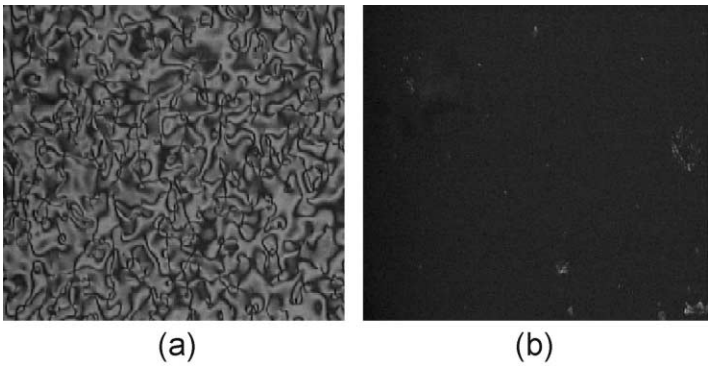


Fig. 1. Optical photomicrographs of (a) **1a**: 93 °C, nematic phase; (b) **2f**: 78 °C, SmA phase; magnification 200×.

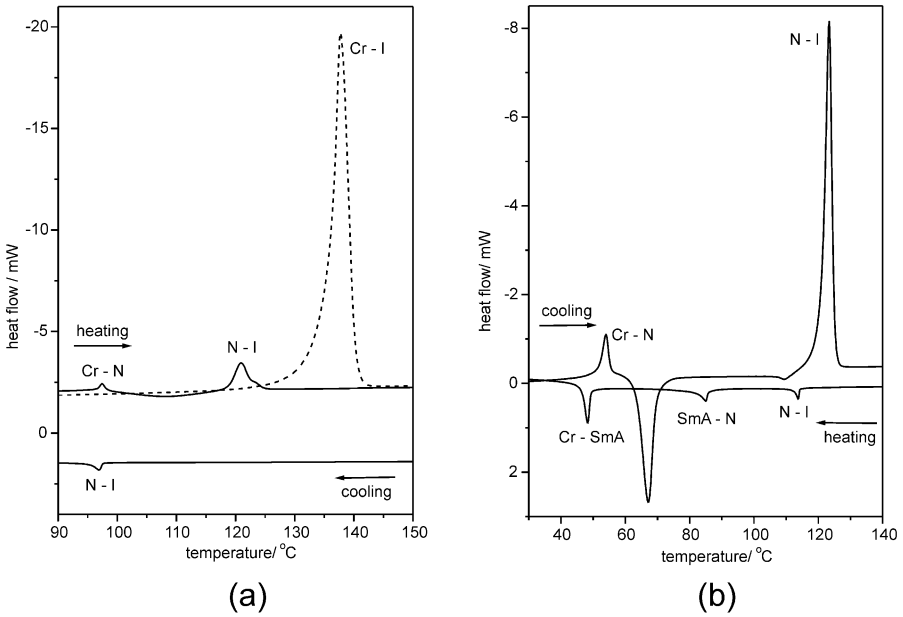


Fig. 2. DSC thermograms of (a) **1a** and (b) **2f**.

peaks were found at 97 and 121 °C for the crystal–nematic phase transition (Cr–N) and the nematic phase-isotropic transition (N–I), respectively, on second heating. The second heating and cooling scans were reproducible. One exothermic peak corresponding to nematic phase was found at 96 °C. **1e** and **1f** did not form a mesophase. In compounds of series **1**, crystallization rate from supercooled species was too slow to be detected by DSC even below room temperature, while all compounds in series 2 displayed the crystallization peaks. In the case of series **2**, most compounds formed nematic and smectic A (SmA) phases, while **2d** and **2e** formed only a nematic phase [19]. From the DSC thermogram for **2f**, one endothermic peak at 56 °C corresponding to the Cr–N transition, was found and another strong peak at 120 °C was found corresponding to N–I transition, on heating. On cooling, the first and second weak peak at 112 and 86 °C were identified to be nematic and SmA phase, respectively, shown in Fig. 2(b).

To reconfirm the phases obtained from DSC and from optical polarizing microscopy, a normal twisted nematic (TN) cell with 4.5 μm cell gap and

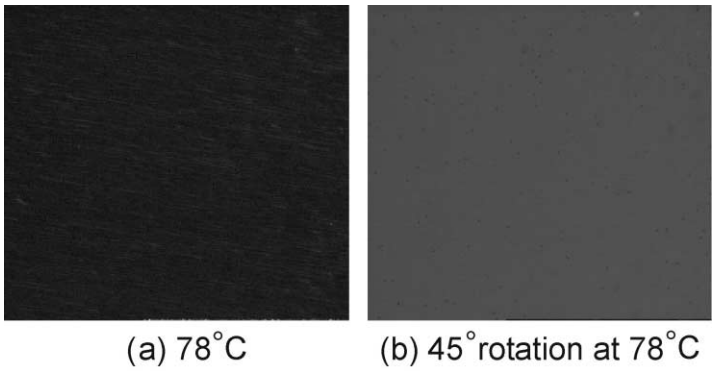


Fig. 3. Electric/optical characteristics by a ferroelectric cell (F-cell): (a) and (b) were a black and a white state without voltage and with rotating the F-cell under two crossed polarizers for **2f**.

a ferroelectric cell (F-cell) were used. When the F-cell at 78 °C, there was no change of transmittance even though an electric field in the range 0–40 V/μm was applied. This means that the molecular orientation was perpendicular to the layer, which indicated a SmA phase. When the F-cell was rotated at 78 °C without applying the electric field under two crossed polarizers, the highest transmittance (white state) was detected when rotated at 45° from the black state as shown in Fig. 3(a) and (b). These results confirm that this compound has only SmA phase, not a SmC phase. The transition temperatures and the mesophase for the compounds of series **1** and **2** are summerized in the Table 2.

Table 2
Phase transition temperature[a] of **1a**–**1f** and **2a**–**2e**

	Cr		SmA		N		I
1a	–	(97)	–	–	•	96 (121)	•
1b	–	–	–	–	•	92	•
1c	•	(74)	–	–	•	101 (125)	•
1d	–	–	–	–	•	86	•
1e	–	–	–	–	–	–	•
1f	–	–	–	–	–	–	–
2a	•	97	•	100	•	135	•
2b	•	98	•	105	•	136	•
2c	•	91	•	98	•	128	•
2d	•	71	–	–	•	105	•
2e	•	65	–	–	•	107	•
2f	•	50 (56)	•	86	•	112	•

[a] Data in parentheses are phase-transition temperatures on heating.

This study focussed on the spiropyran-containing liquid crystal compounds, which have the chiral SmC* mesophasic character and which satisfy the chirooptical properties essential for developing liquid crystal optical switch (LCOS). Further work is in progress.

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