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Synthesis and characterization of new liquid crystalline materials containing a non-activated arylazoindolinobenzospiropyranyl group as a chiral unit. Part II†

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Two series of new liquid crystalline compounds containing a non-activated arylazoindolinobenzospiropyran, ABP-SPAB **1a–1e** (series **1**) and SPAP-ABPC **2a–2e** (series **2**), have been synthesized. These LC dyes were characterized by a differential scanning calorimetry polarizing optical microscopy, X-ray diffraction and electro-optical measurements. All but one of the series **1** compounds examined exhibit monotropic second and/or third transition liquid crystal phases on cooling from the isotropic liquid. In particular, ABP-SPAB **1b** shows a monotropic SmC phase, in addition to a SmA phase. In series **2**, most of the compounds exhibit a monotropic nematic phase on cooling. SPAP-ABPC **2c** forms an enantiotropic nematic phase and a monotropic SmA phase; **2e** shows enantiotropic nematic and SmA phases.

1. Introduction

Materials which can be reversibly written on and read by light provide an important technology in our digital age. Development of these materials requires the discovery of compounds that exhibit two distinct chemical or physical forms that are interconverted and sensed by light without destruction. Organic photochromic compounds have obvious potential for such light-controlled devices. Photochromic spiropyran dyes have attracted wide attention in many applications in optical switching, high-density optical data storage, holographic system and optical computing [1, 2]. Most studies have focused on derivatives having an electron-withdrawing group such as the NO_2 group substituted in the 6-position of the spiropyran to utilize the photochemical ring-opening reaction due to its stabilized merocyanine form. Recently, however, our group has paid attention to the so-called non-activated spiropyrans which lack a strong electron-withdrawing substituent, and has been studying those which have several applications [3–6]. A few examples of spiropyran-containing mesogens have been reported. Krongauz and co-workers proposed a quasi-liquid crystal phase with physical properties analogous to those of a nematic phase [7, 8]. Other groups reported works which incorporated the spiropyran unit as photochromic or thermochromic side chains in polymer nematic liquid crystals and cyclic siloxanes [9, 10]. Recently, we reported a study of the optical resolution and circular dichroism of the non-activated spiropyran dye, 6-(*p*-chlorophenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2, 2′-indoline] [11]. We have also reported the synthesis and characterization of novel mesogens incorporating a non-activated spiropyran 4′-octyloxybiphenyl-4-carboxylate derivative, which was found to exhibit a monotropic SmC phase [12].

These LC 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

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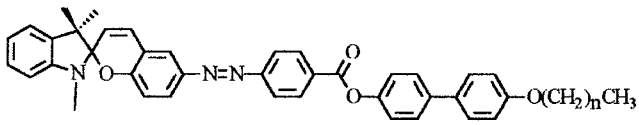
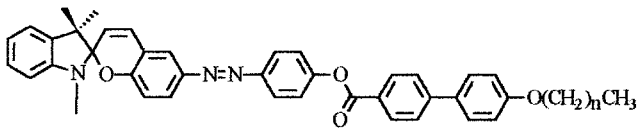
aligned nematic liquid crystal with circularly polarized light would induce a cholesteric phase, whereas irradiation of the induced cholesteric phase with unpolarized light of the same wavelength would restore the nematic phase by photoracemization of the dopant. Spiropyran (SP) is inherently a chiral 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 and (*S*)-SP at equal rates, and under such conditions of the photostationary state the SP exists as rapidly interconverting enantiomers [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 favours the SP component. Because this light-induced interconversion can be sensed from the change in the optical rotatory power of the liquid crystal, it may serve as the basis for the liquid crystal optical switch. Our research has focused on several non-activated spyropyrans having the chiroptical properties essential for a liquid crystal optical switch (LCOS) based on photoresolution [14–16]. For the development of a ferroelectric liquid crystal optical switch, we have recently expanded our research into smectic C (SmC) mesogens incorporating a non-activated spiropyran unit. In this report we describe the synthesis and characterization of the two series of compounds ABP-SPAB **1a–1e** and SPAP-ABPC **2a–2e**.



ABP-SPAB 1a~1e (n=5~9)



SPAP-ABPC 2a~2e (n=5~9)

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 solution on a Varian 300 NMR spectrophotometer. Chemical shifts are reported in δ (ppm) relative to tetramethylsilane as the internal standard. High resolution FAB mass spectra were obtained from the Basic Science Research Institute of Korea University. The DSC thermograms of the compounds were obtained using a DuPont 910 Thermal Analyser calibrated with indium, under N_2 at a heating/cooling rate of 10°C min^{-1}. The optical textures and thermal transitions were obtained using a Nikon Labophot-2 polarizing microscope equipped with a Mettler FP82HT hot stage. An X-ray diffractometer, 3 kW–8 eV, was used for studying the phase transitions. 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 magnetics placed inside the oven. A twisted nematic (TN) cell and a 4 μm cell with planar alignment were made by a general method using the commercial alignment material RN1199 whose pretilt angle was ~1°. Two-side 90° twisted rubbing, and one-side rubbing treatments 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.

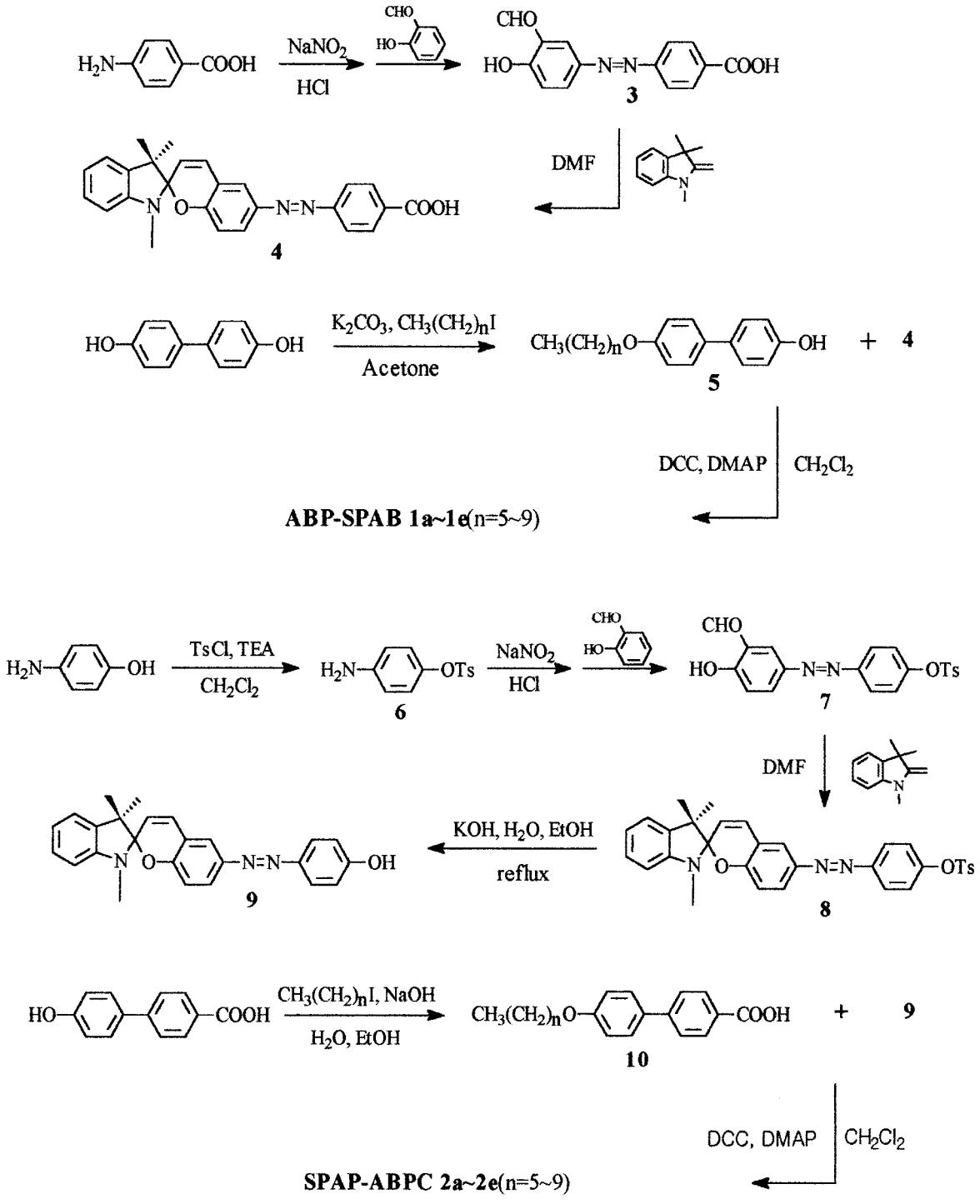
2.3. *Synthesis of ABP-SPAB compounds **1a–1e*** (see the scheme)

2.3.1. *4-(3-Formyl-4-hydroxyphenylaz o)benzoic acid*

A solution of $NaNO_2$ (0.8 g, 11.6 mmol) in H_2O (20 ml) was added to salicylaldehyde (1.4 g, 10.9 mmol) in aq. NaOH (0.9 g), with the temperature maintained at 5°C. The resulting solution was added dropwise to a solution of 4-aminobenzoic acid (1.6 g, 11.6 mmol) in aq. HCl (0.8 g) at 0°C. Following the addition, the reaction mixture was stirred for 1 h at room temperature and the precipitate was filtered and washed three times with distilled water. Recrystallization from acetone afforded 2.1 g of a red–brown solid; yield 69%, m.p. 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. *[1′,3′,3′-Trimethylspiro(2H-1-benzopyran-2, 2′-indoline)-6-yl]azobenzoic acid **4***

To a solution of 4-(3-formyl-4-hydroxyphenylazo)-benzoic acid (1.9 g, 13.5 mmol) in 40 ml of DMF, 2-methylene-1,3,3-trimethylindolin e (0.95 g, 10.8 mmol) was added. The mixture was stirred for 5 h at room temperature. After the reaction was complete, the mixture was poured into 100 ml of distilled water and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and the solvent evaporated. Recrystallization from hexane ethyl acetate gave 3.4 g of light-red crystal; yield 73%, m.p. 228°C. ^{1}H NMR



Scheme. Synthetic routes to ABP-SPAB and SPAP-ABPC compounds.

(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. *4-(4-Nonyloxyphenyl)phenol* **5**

The following procedure is representative. To 4,4′-biphenol (1.0 g, 5.37 mmol) in 60 ml of acetone, K_2CO_3 (0.74 g) was added and the mixture heated under reflux. After 30 min, iodononane (0.24 ml, 1.34 mmol) was added to this solution and the reflux maintained for

10 h. The remaining solid was filtered off and the filtrate evaporated *in vacuo* and purified by column chromatography on silica gel (10 : 1 hexane/ethyl acetate), giving 0.29 g of white solid; yield 72%, m.p. 124°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H), 1.14–1.41 (m, 12H), 1.80 (m, 2H), 3.98 (t, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 7.39 (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H).

2.3.4. *General procedure for the esterification reaction of compounds **4** and **5***

The following procedure is representative. To a solution of 4-(4-nonyloxyphenyl)phenol (0.10 g, 0.32 mmol) and **4** (0.20 g, 0.47 mmol) in 30 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 its TLC pattern monitored 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), giving 0.14 g of an orange solid, **1e**. The product was further purified by recrystallization from acetone.

4′-Hexyloxybiphenyl-4-yl [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl]azobenzoate ***1a***. Yield 65%, m.p. 169°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H), 1.21 (s, 3H), 1.29–1.44 (m, 6H), 1.34 (s, 3H), 1.82 (m, 2H), 2.78 (s, 3H), 4.01 (t, 2H), 5.82 (d, $J = 10.5$ Hz, 1H), 6.57 (d, 1H), 6.87 (d, $J = 8.8$ Hz, 1H), 6.89 (t, 1H), 6.98 (d, $J = 8.7$ Hz, 2H), 7.00 (d, 1H), 7.10 (d, 1H), 7.21 (t, 1H), 7.29 (d, $J = 8.7$ Hz, 2H), 7.52 (d, 2H), 7.61 (d, 2H), 7.76 (s, 1H), 7.82 (d, 1H), 7.97 (d, $J = 9.0$, 2H), 8.35 (d, 2H). MS *m/z* 678 (M^+, 100), 366 (57), 312 (32), 292 (17), 186 (45), 159 (62), 120 (88). High resolution MS: calculated for $C_{44}H_{43}N_3O_4$ 678.4712; found 678.4701.

4′-Heptyloxybiphenyl-4-yl [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl]azobenzoate ***1b***. Yield 72%, m.p. 136°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 3H), 1.21 (s, 3H), 1.31–1.44 (m, 8H), 1.34 (s, 3H), 1.82 (m, 2H), 2.78 (s, 3H), 3.99 (t, 2H), 5.82 (d, $J = 10.3$ Hz, 1H), 6.57 (d, 1H), 6.88 (d, $J = 8.7$ Hz, 1H), 6.88 (t, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 6.99 (d, 1H), 7.09 (d, 1H), 7.19 (t, 1H), 7.27 (d, $J = 8.7$ Hz, 2H), 7.56 (d, 2H), 7.61 (d, 2H), 7.78 (s, 1H), 7.82 (d, 1H), 7.97 (d, $J = 8.9$, 2H), 8.35 (d, 2H). MS *m/z* 692 (M^+, 100), 380 (83), 312 (24), 292 (18), 186 (51), 159 (69), 120 (83). High resolution MS: calculated for $C_{45}H_{45}N_3O_4$ 692.3878; found 692.3852.

4′-Octyloxybiphenyl-4-yl [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl]azobenzoate ***1c***. Yield 75%, m.p. 128°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, 3H), 1.21 (s, 3H), 1.30–1.46 (m, 10H), 1.34 (s, 3H), 1.89 (m, 2H), 2.77 (s, 3H), 4.01 (t, 2H), 5.82 (d, $J = 10.2$ Hz, 1H), 6.57 (d, 1H), 6.87 (d, $J = 8.8$ Hz, 1H), 6.88 (t, 1H), 6.97 (d, 1H), 6.99 (d, $J = 8.8$ Hz, 2H), 7.10 (d, 1H), 7.19 (t, 1H), 7.27 (d, $J = 8.7$ Hz, 2H), 7.54 (d, 2H), 7.63 (d, 2H), 7.79 (s, 1H), 7.81 (d, 1H), 7.99 (d, $J = 9.0$, 2H), 8.35 (d, 2H). MS *m/z* 706 (M^+, 100), 394 (68), 312 (34), 292 (28), 186 (47), 159 (72), 120 (84). High resolution MS: calculated for $C_{46}H_{47}N_3O_4$ 706.3030; found 706.3065.

4′-Nonyloxybiphenyl-4-yl [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl]azobenzoate ***1d***. Yield 68%, m.p. 124°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.20 (s, 3H), 1.29–1.46 (m, 12H), 1.34 (s, 3H), 1.90 (m, 2H), 2.77 (s, 3H), 4.00 (t, 2H), 5.82 (d, $J = 10.2$ Hz, 1H), 6.57 (d, 1H), 6.86 (d, $J = 8.8$ Hz, 1H), 6.88 (t, 1H), 6.98 (d, $J = 8.8$ Hz, 2H), 6.99 (d, 1H), 7.10 (d, 1H), 7.21 (t, 1H), 7.28 (d, $J = 8.8$ Hz, 2H), 7.52 (d, 2H), 7.61 (d, 2H), 7.75 (s, 1H), 7.81 (d, 1H), 7.97 (d, $J = 8.9$, 2H), 8.35 (d, 2H). MS *m/z* 720 (M^+, 100), 408 (73), 312 (27), 292 (18), 186 (52), 159 (68), 120 (88). High resolution MS: calculated for $C_{47}H_{49}N_3O_4$ 720.3801; found 720.3812.

4′-Decyloxybiphenyl-4-yl [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl]azobenzoate ***1e***. Yield 69%, m.p. 119°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H), 1.21 (s, 3H), 1.30–1.45 (m, 14H), 1.34 (s, 3H), 1.90 (m, 2H), 2.77 (s, 3H), 3.98 (t, 2H), 5.82 (d, $J = 10.2$ Hz, 1H), 6.58 (d, 1H), 6.87 (d, $J = 8.7$ Hz, 1H), 6.89 (t, 1H), 6.98 (d, $J = 8.7$ Hz, 2H), 6.99 (d, 1H), 7.09 (d, 1H), 7.21 (t, 1H), 7.29 (d, $J = 8.8$ Hz, 2H), 7.52 (d, 2H), 7.60 (d, 2H), 7.76 (s, 1H), 7.82 (d, 1H), 7.97 (d, $J = 9.0$, 2H), 8.36 (d, 2H). MS *m/z* 734 (M^+, 100), 422 (68), 312 (19), 292 (28), 186 (52), 159 (69), 120 (85). High resolution MS: calculated for $C_{48}H_{51}N_3O_4$ 734.2791; found 734.2817.

2.4. *Synthesis of SPAP-ABPC compounds **2a–2e*** (see the scheme)

2.4.1. *4-(p-Toluenesulphonyloxy)aniline* ***6*** [17]

p-Aminophenol (2.0 g, 18.3 mmol) was dissolved in methylene chloride (70 ml). Triethylamine (2.3 g, 21.9 mmol) and *p*-toluenesulphony chloride (2.0 g, 18.3 mmol) were added to the solution and it was stirred for 3 h. The reaction mixture was washed five times with H_2O, and the separated organic layer was dried over anhydrous $MgSO_4$ and evaporated. The crude product was recrystallized from acetone to give 4.1 g of a white–grey solid; yield 86%, m.p. 117°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (s, 3H), 6.51 (d, $J = 8.7$ Hz, 2H), 6.73 (d, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.68 (d, 2H).

2.4.2. *5-(p-Toluenesulphonyloxyphenylazo)-salicylaldehyde* ***7***

To a solution of 4-(*p*-toluenesulphonyloxy)aniline (4.8 g, 18.2 mmol) in aq. HCl (1.2 g, 33.8 mmol) cooled to 0°C was added a solution of $NaNO_2$ (1.3 g, 18.2 mmol) in H_2O (10 ml). The resulting cold solution was added

slowly to salicylaldehyde (2.7 g, 21.0 mmol) in 20% aq. NaOH (1.4 g, 33.8 mmol), and kept at 0°C. After standing for 2 h, the mixture was filtered and the residue recrystallized from acetone to give 5.5 g of an orange solid; yield 75%, m.p. 98°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.04 (d, $J = 8.7$ Hz, 2H), 7.12 (d, 1H), 7.32 (d, $J = 9.0$ Hz, 2H), 7.76 (d, $J = 8.7$ Hz, 2H), 7.78 (d, $J = 9.0$ Hz, 2H), 8.05 (d, 1H), 8.31 (s, 1H).

2.4.3. *6-(p-Toluenesulphonyloxyphenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline]* ***8***

The compound **8** was prepared by the same procedure as in § 2.2.2. The crude product was purified by column chromatography on silica gel (15 : 1 hexane/ethyl acetate) giving 5.64 g of a light-red solid; yield 72%, m.p. 105°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 3H), 1.34 (s, 3H), 2.35 (s, 3H), 2.76 (s, 3H), 5.79 (d, $J = 10.2$ Hz, 1H), 6.82 (d, $J = 8.7$ Hz, 1H), 6.87 (t, 1H), 6.96 (d, 1H), 7.04 (d, $J = 8.7$ Hz, 2H), 7.10 (d, 1H), 7.19 (t, 1H), 7.32 (d, $J = 9.0$ Hz, 2H), 7.66 (s, 1H), 7.74 (d, 1H), 7.76 (d, 2H), 7.79 (d, 2H).

2.4.4. *6-(p-Hydroxyphenylazo)-1′,3′,3′-trimethylspiro-[2H-1-benzopyran-2,2′-indoline]* ***9***

Compound **9** was prepared by the following method. To a solution of **8** (2.0 g, 3.43 mmol) in ethanol (80 ml) was added a solution KOH (0.29 g, 5.14 mmol) in H_2O (10 ml) and the mixure heated under reflux for 8 h. The reaction mixture was evaporated to dryness and purified by column chromatography on silica gel (20 : 1 hexane/ethyl acetate) giving 1.01 g of dark green solid; yield 68%, m.p. 88°C. ^{1}H 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).

2.4.5. *4′-Alkyloxybiphenyl-4-carboxylic acid* ***10***

The following procedure is representative. To a solution of 4-(4′-hydroxybiphenyl)carboxylic acid (1 g, 4.66 mmol) in ethanol (60 ml) was added a solution of sodium hydroxide (0.22 g, 5.59 mmol) in H_2O (40 ml) followed by iodo-octane (1.19 g, 4.66 mmol). The mixture was heated under reflux for 8 h and cooled to room temperature. The filtered solid was acidified to pH 3 ~ 4 with 6M HCl. The mixture was extracted with ethyl acetate and washed with H_2O. The organic layer was dried over anhydrous $MgSO_4$ and evaporated, giving 0.71 g of white solid; yield 47%, m.p. 162°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, 3H), 1.25–1.46 (m, 12H), 1.80 (m, 2H), 4.01 (t, 2H), 6.99 (d, $J = 9.0$ Hz, 2H), 7.58 (d, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 8.12 (d, $J = 8.4$ Hz, 2H).

2.4.6. *General procedure for the esterification reaction of compounds* ***9*** *and* ***10***

The desired compounds were prepared according to the same method described in § 2.3.4. The crude products were purified by column chromatography on silica gel (20 : 1 hexane/ethyl acetate).

[6-(1″-Phenylazo)-1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)]-4″-yl 4′-hexyloxybiphenyl-4-carboxylate ***2a***. Yield 71%, m.p. 208°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.20 (s, 3H), 1.23–1.48 (m, 6H), 1.33 (s, 3H), 1.83 (m, 2H), 2.76 (s, 3H), 3.99 (t, 2H), 5.80 (d, $J = 10.3$ Hz, 1H), 6.57 (d, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 6.87 (t, 1H), 6.98 (d, 1H), 7.08 (d, $J = 8.8$ Hz, 2H), 7.10 (d, 1H), 7.20 (t, 1H), 7.39 (d, $J = 9.0$ Hz, 2H), 7.61 (d, 2H), 7.71 (s, 1H), 7.74 (d, $J = 8.7$ Hz, 2H), 7.77 (d, 1H), 7.96 (d, 2H), 8.26 (d, 2H). MS *m/z* 678 (M^+, 12), 663 (8), 397 (45), 278 (17), 159 (100), 144 (34), 120 (88). High resolution MS: calculated for $C_{44}H_{43}N_3O_4$ 678.4712; found 678.4734.

[6-(1″-Phenylazo)-1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)]-4″-yl 4′-heptyloxybiphenyl-4-carboxylate ***2b***. Yield 70%, m.p. 202°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, 3H), 1.20 (s, 3H), 1.26–1.48 (m, 8H), 1.34 (s, 3H), 1.83 (m, 2H), 2.77 (s, 3H), 4.02 (t, 2H), 5.80 (d, $J = 10.2$ Hz, 1H), 6.56 (d, $J = 7.7$ Hz, 1H), 6.84 (d, $J = 9.0$ Hz, 1H), 6.87 (t, 1H), 6.98 (d, 1H), 7.01 (d, $J = 8.7$ Hz, 2H), 7.10 (d, 1H), 7.20 (t, 1H), 7.38 (d, $J = 9.0$ Hz, 2H), 7.61 (d, 2H), 7.71 (s, 1H), 7.74 (d, 1H), 7.96 (d, $J = 8.4$ Hz, 2H), 7.96 (d, 2H), 8.29 (d, 2H). MS *m/z* 692 (M^+, 10), 677 (8), 397 (32), 292 (21), 159 (100), 144 (18), 120 (72). High resolution MS: calculated for $C_{45}H_{45}N_3O_4$ 692.3878; found 692.3859.

[6-(1″-Phenylazo)-1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)]-4″-yl 4′-octyloxybiphenyl-4-carboxylate ***2c***. Yield 65%, m.p. 186°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H), 1.20 (s, 3H), 1.26–1.49 (m, 10H), 1.34 (s, 3H), 1.81 (m, 2H), 2.77 (s, 3H), 3.98 (t, 2H), 5.83 (d, $J = 10.5$ Hz, 1H), 6.55 (d, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 6.87 (t, 1H), 6.97 (d, 1H), 7.01 (d, $J = 8.8$ Hz, 2H), 7.10 (d, 1H), 7.19 (t, 1H), 7.39 (d, $J = 9.1$ Hz, 2H), 7.68 (d, 2H), 7.72 (s, 1H), 7.74 (d, $J = 8.7$ Hz, 2H), 7.75 (d, 1H), 7.94 (d, 2H), 8.26 (d, 2H). MS *m/z* 706 (M^+, 12), 691 (8), 397 (29), 306 (52), 159 (100), 144 (17), 120 (90). High resolution MS: calculated for $C_{46}H_{47}N_3O_4$ 706.3030; found 706.3053.

[6-(1″-Phenylazo)-1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)]-4″-yl 4′-nonyloxybiphenyl-4-carboxylate ***2d***. Yield 61%, m.p. 169°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, 3H), 1.20 (s, 3H), 1.26–1.47 (m, 12H), 1.34 (s, 3H), 1.83 (m, 2H), 2.77 (s, 3H), 4.02 (t, 2H), 5.81 (d, $J = 10.5$ Hz, 1H), 6.56 (d, $J = 7.3$ Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 1H), 6.88 (t, 1H), 6.98 (d, 1H), 7.03 (d, $J = 8.8$ Hz, 2H), 7.09 (d, 1H), 7.20 (t, 1H), 7.39 (d, $J = 9.1$ Hz, 2H), 7.63 (d, 2H), 7.71 (s, 1H), 7.74

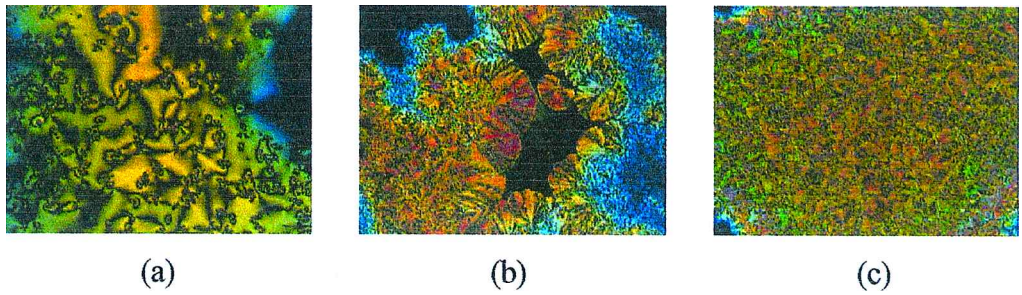


Figure 1. Optical photomicrographs of **1b** on cooling from isotropic liquid: (*a*) nematic phase at 187°C, (*b*) SmA phase at 162°C, (*c*) SmC phase at 102°C; magnification 200×.

(d, 1H), 7.85 (d, $J = 8.7$ Hz, 2H), 7.96 (d, 2H), 8.32 (d, 2H). MS *m/z* 706 (M^+, 12), 705 (8), 397 (27), 320 (43), 159 (100), 144 (19), 120 (85). High resolution MS: calculated for $C_{47}H_{49}N_3O_4$ 720.3801; found 720.3820.

[6-(1″-Phenylazo)-1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)]-4″-yl 4′-decyloxybiphenyl-4-carboxylate ***2e***. Yield 79%, m.p. 157°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H), 1.20 (s, 3H), 1.25–1.49 (m, 14H), 1.34 (s, 3H), 1.83 (m, 2H), 2.77 (s, 3H), 4.02 (t, 2H), 5.80 (d, $J = 10.5$ Hz, 1H), 6.56 (d, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 6.87 (t, 1H), 6.98 (d, 1H), 7.01 (d, $J = 8.7$ Hz, 2H), 7.10 (d, 1H), 7.20 (t, 1H), 7.38 (d, $J = 9.1$ Hz, 2H), 7.61 (d, 2H), 7.71 (s, 1H), 7.72 (d, $J = 8.7$ Hz, 2H), 7.77 (d, 1H), 7.96 (d, 2H), 8.26 (d, 2H). MS *m/z* 734 (M^+, 10), 719 (8), 397 (21), 334 (38), 159 (100), 144 (19), 120 (90). High resolution MS: calculated for $C_{48}H_{51}N_3O_4$ 734.2791; found 734.2775.

3. Results and discussion

The characterization of liquid crystal phases exhibited by these spiropyran moieties was made by differential scanning calorimetry (DSC), optical polarizing microscopy (POM), X-ray diffraction and by electro-optical measurements. Most of the compounds studied exhibited mesomorphic behaviour on the first cooling and the subsequent heating cycle. Because of the thermo- and photo-chromic properties of the spiropyran dyes, the existence of a small portion of the ring-opened merocyanine species may not be negligible at high temperature [18]. However, it is supposed that the presence of mesophase during the first cooling stage was the result of reorientation of the spiropyran molecules in the isotropic liquid. The quantity of ring-opened merocyanine in solid state is negligible.

In series **1** compounds **1a**, **1b**, **1d** and **1e** formed both monotropic nematic and smectic phases, whereas **1c** formed only a nematic phase. The POM study of **1b** showed a nematic, SmA and SmC phase on cooling from the isotropic phase, as shown in figure 1 [19, 20]. The mesophase formed by **1d** was shown by XRD to be a SmC phase with unknown texture.

From the DSC thermogram obtained from **1b** (figure 2) the first and second weak peaks at 220 and 179°C on cooling were identified to be a nematic and a SmA phase, respectively. Upon lowering the temperature further, the next transition at 107°C correponded to the appearance of a SmC phase. The strong peak at 90°C marked the transition to the crystal phase. **1d** also exhibited an isotropic → nematic → SmA → SmC phase sequence with decreasing temperature. The heats of transition of the N–SmA exotherm were 0.011–0.083 kJ g^{-1} in series **1** and 0.293–0.564 kJ g^{-1} in series **2**. The N–SmA exotherm was unusually much smaller than the SmA–SmC exotherm; 0.063 vs. 0.273 and 0.011 vs 0.137 kJ g^{-1} for **1b** and **1d**, respectively. Comparing the exothermal peaks in figures 2 and 3, the heat of transition of the N–SmA exotherm for **1b** (0.064 kJ g^{-1}) was one of sixth of that for **2e** (0.357 kJ g^{-1}). Most of the compounds in series **2** exhibited a monotropic nematic phase.

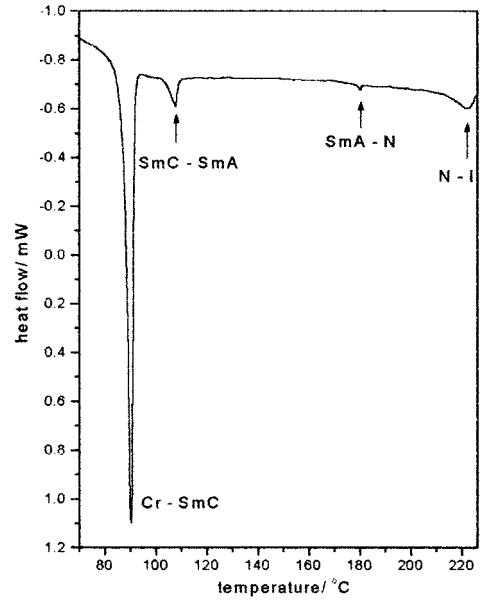


Figure 2. DSC thermogram of ABP-SPAB **1b** on cooling from isotropic liquid.

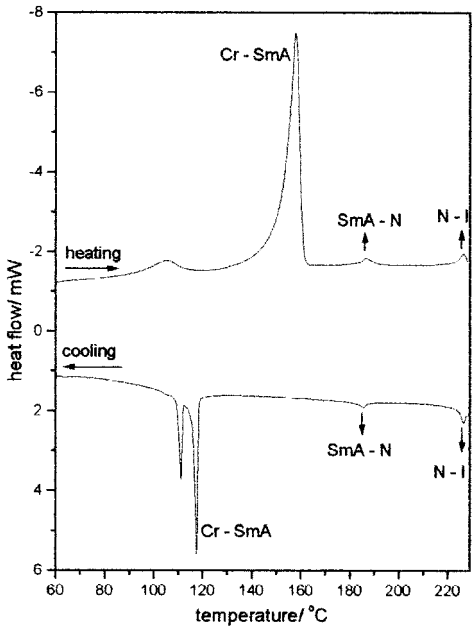


Figure 3. DSC thermogram of SPAP-ABPC **2e**.

2c formed an enantiotropic nematic phase and a monotropic SmA phase on cooling. In addition, **2e** was found to form both an enantiotropic nematic and a SmA phase with a homeotropic domain texture (figure 3).

Series **1** compounds formed only a monotropic liquid crystal phase; results obtained by DSC were confirmed XRD as follows. Figure 4 shows X-ray diffractograms obtained at three different temperatures from a cooling scan from the isotropic phase for ABP-SPAB **1b**. Figure 4 (*a*) shows a diffuse pattern at 180°C, on applying a magnetic field in the 225° direction, indicating a nematic phase. Figures 4 (*b*) and 4 (*c*) show the intense peaks obtained at 150°C and 100°C, which indicate SmA and SmC phases, respectively. As shown in figure 4 (*b*), the molecules were perpendicular to the layer for the SmA phase; molecule tilt in the layer, which can be deduced from the diffraction pattern in figure 4 (*c*), indicates the SmC phase.

We also found by XRD that there was no molecular alignment at 220°C for ABP-SPAB **1d**, indicating the isotropic phase. The diffuse pattern indicates the nematic phase appeared at 170°C, and an intense peak with molecular tilt to the layer, confirming the SmC phase, appeared at 125°C. The existence of a SmA phase could not be confirmed by XRD. It was, however, identified by a 4 μm cell experiment with planar alignment.

In order to confirm the phases obtained by DSC and POM for SPAP-ABPC **2e**, we used a normal twisted nematic (TN) cell with 4.5 μm cell gap and a 4 μm cell with planar alignment applied by one-side rubbing with the same cell gap. As shown in figures 5 (*a*) and 5 (*b*), the TN cell showed the white state at 200°C without voltage, but showed the black state at the same temperature with 15 V voltage. The presence of a nematic phase at 200°C may be deduced. In the case of the 4 μm cell with planar alignment at 150°C, there was no change of transmittance even under an electric field in the range of 0–40 V μm^{-1}. The molecular orientation was therefore perpendicular to the layer, indicating a SmA phase. On rotating the cell at 150°C with no electric field under the two crossed polarizers, the highest transmittance (white state) was found on rotating 45° to the angle of the black state, as shown in figures 5 (*c*) and 5 (*d*). These results confirmed that this compound has only a SmA phase, and no SmC phase.

It was found that a few compounds exhibited the enantiotropic nematic phase after repeated measurements, because a small amount of ring-opened merocyanine (transformed from ring-closed spiropyran) remained on cooling after the spiropyran melted into the isotropic liquid at the relatively high temperature. Regardless of chain length, most compounds examined in this study

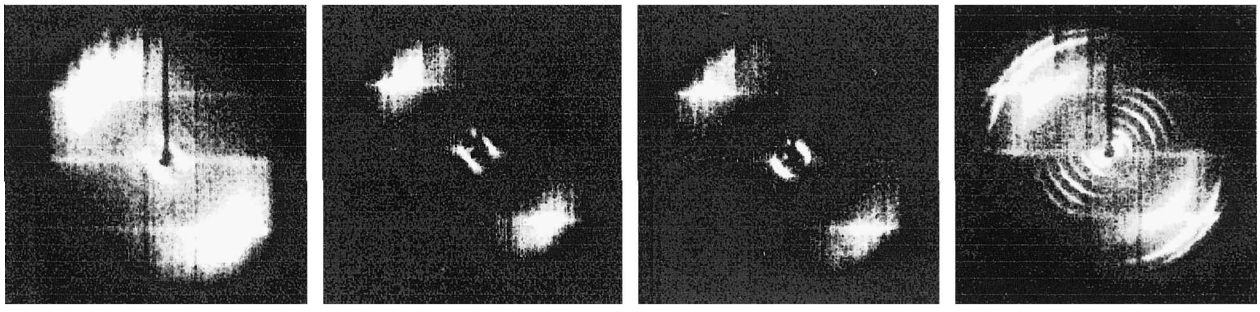


Figure 4. Phase transition by XRD from the cooling scan for **1b** (*a*) 180°C, nematic; (*b*) 150°C, SmA; (*c*) 100°C, SmC; (*d*) 80°C, crystalline at 102°C.

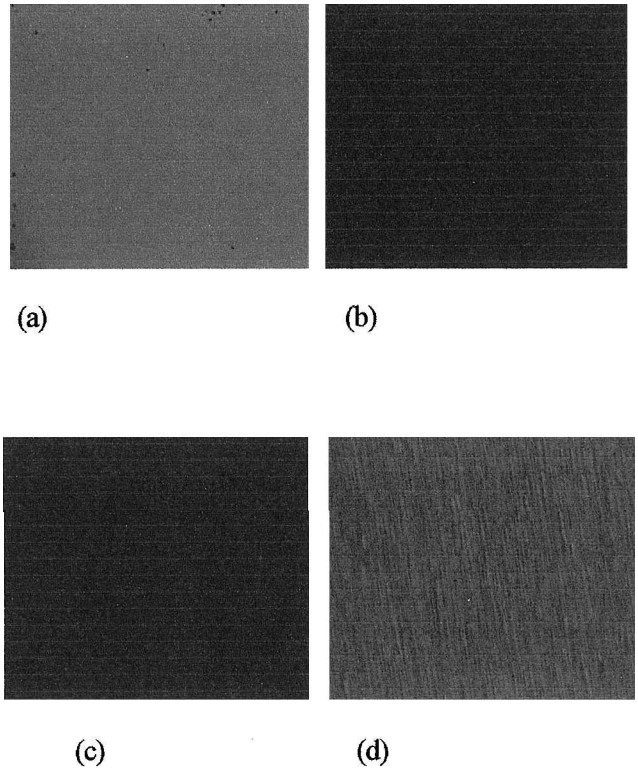


Figure 5. Electro-optical characteristics of a normal twisted nematic (TN) cell and a 4 μm cell with planar alignment. (*a*) TN cell white state at 200°C and 15 V voltage; (*b*) TN cell black state at 200°C and zero voltage. (*c*) 4 μm planar aligned cell black state at 150°C and zero voltage; (*d*) as (*c*), white state with 45° rotation under crossed polarizers.

were formed 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–1e** and SPAP-ABPC **2a–2e** ($n = 5$–9) are shown in the table.

4. Conclusions

New liquid crystalline materials incorporating a non-activated arylazospiropyran unit have been synthesized and their properties studied. For the mesophases obtained from these LC dyes, DSC and POM studies are coincident with XRD and electro-optical analysis. As a result of the influence of the terminal alkoxy group, most of the compounds have been shown to form both the nematic and smectic phases. Among the compounds, ABP-SPAB **1b** and **1d** were showed monotropic nematic, SmA and SmC transition phase sequences on cooling; **1c** showed only a nematic phase on cooling the isotropic liquid. The N–SmA exotherm was unusually much smaller than the SmA–SmC exotherm, 0.063 vs. 0.273, and 0.011 vs. 0.137 kJ g^{-1} for **1b** and **1d**, respectively. Most of the SPAP-ABPC series exhibited a monotropic nematic phase except for **2c** and **2e**, with an even carbon number, which were shown to have an enantiotropic nematic phase, and an enantiotropic nematic and SmA phase, respectively. The SPAP-ABPC compounds have higher temperature phase transitions than the ABP-SPAB compounds by 30–70 degrees; for some compounds, we had difficulty in obtaining perfect DSC curves due to the instability of the azo group at high temperatures. These results show that (1) liquid crystal behaviour is influenced by the diversity of the carbon number and mesogenic unit, (2) molecular architecture affects the interaction with neighbouring molecules. The results also indicate that mesogens incorporating the non-activated spiropyran moiety have been found, which satisfy the chiro-optical properties essential for developing a liquid crystal optical switch. However, due to the relatively high transition temperatures caused by the biphenyl unit, it is unsuitable for real applications. We are therefore seeking an efficient spiropyran mesogen that will surmount this defect.

Table. Phase transition temperature of 4′-alkyloxybiphenyl-4-yl [1′,3′,3′-trimethylspiro(2H-1-benzopyran-2,2′-indoline)-6-yl]-azobenzoate, ABP-SPAB (AS) **1a–1e**, and [6-(1″-phenylazo)-1′,3′,3′-trimethylspiro(2H-1-benzopyran-2-2′-indoline)]-4″-yl 4′-alkyloxybiphenyl-4-carboxylate, SPAP-ABPC (SA) **2a–2e** on cooling from isotropic liquid.

Compound	Cr		SmC		SmA		N		I
1a	●	63	—		●	103	●	170	●
1b	●	90	●	113	●	172	●	197	●
1c	●	79	—		—		●	187	●
1d	●	110	●	131	●	148	●	192	●
1e	●	118	—		●	129	●	181	●
2a	●	121	—	—	—	—	●	220	●
2b	●	132	—	—	—	—	●	215	●
2c	●	113	—	—	●	187	●	224 (193)[a]	●
2d	●	149	—	—	—	—	●	212	●
2e	●	111	—	—	●	182 (178)[a]	●	221 (218)[a]	●

[a] Phase transition temperature on heating: melting points were 186 and 157°C for **2c** and **2e**, respectively.

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References

[1] Brown, G. H. (editor), 1971, *Photochromism* (New York: Wiley).
[2] Dürr, H., and Bouas-Laurent, H. (editors), 1990, *Photochromism–Molecules and Systems* (Amsterdam: Elsevier).
[3] Keum, S.-R., Lee, K.-B., Kazmaier, P. M., and Buncel, E., 1994, *Tetrahedron Lett.*, **37,** 1105.
[4] Keum, S.-R., Choi, Y.-K., Kim, S.-H., and Yoon, C.-M., 1999, *Dyes Pigm.*, **41,** 41.
[5] Aramaki, S., and Atkinson, G. H., 1992, *J. Am. chem. Soc.*, **114,** 438.
[6] Zhang, J. Z., Schwartz, B. J., King, J. C., and Harris, C. B., 1992, *Tetrahedron, Lett.*, **37,** 1015.
[7] Shvartsman, F. P., and Krongauz, V. A., 1984, *J. phys. Chem.*, **88,** 6648.
[8] Shvartsman, F. P., Cabrera, I. R., Weis, A. L., Wachtel, E. J., and Krongauz, V. A., 1985, *J. phys. Chem.*, **88,** 6448.
[9] Yitzchaik, S., Cabrera, I., Buchholtz, F., and Kongauz, V., 1990, *Macromolecules*, **23,** 707.
[10] Natarajan, L. V., Bunning, T. J., and Kim, S. Y., 1994, *Macromolecules*, **27,** 7248.
[11] Keum, S.-R., Lee, M.-J., Swansburg, S., Buncel, E., and Lemieux, R. P., 1998, *Dyes Pigm.*, **39,** 383.
[12] Swansburg, S., Choi, Y.-K., Keum, S.-R., Buncel, E., and Lemieux, R. P., 1998, *Liq. Cryst.*, **24,** 341.
[13] Keum, S.-R., and Lee, M.-J., 1999, *Bull. Korean chem. Soc.*, **20,** 1464.
[14] Rau, H., 1983, *Chem. Rev.*, **83,** 535.
[15] Zhang, Y., and Schuster, G. B., 1994, *J. org. Chem.*, **59,** 1855.
[16] Lemieux, R. P., and Schuster, G. B., 1993, *J. org. Chem.*, **58,** 100.
[17] Kurita, K., 1974, *Chem. Ind.* (London), 345.
[18] Hattori, Hu., and Uryu, T., 1999, *Liq. Cryst.*, **26,** 1085.
[19] Gray, G. W., and Goodby, J. W. G., 1984, *Smectic Liquid Crystals* (London: Leonard Hill).
[20] Demus, D., and Richter, L. (editors), 1978, *Textures of Liquid Crystals* (New York, Weinheim: VCH).