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Synthesis and mesomorphic properties of new liquid crystalline compounds

VIII. Indolinbenzospiropyranyl aryliminobenzoates†

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A series of new liquid crystalline compounds, indolinbenzospiropyranyl aryliminobenzoates, **1a–d**, have been synthesized and their mesomorphic properties characterized. Analysis by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction showed that the benzoates **1a** and **1d** form a monotropic mesophase, whereas **1b** and **1c** show an enantiotropic mesophase. Enantiomorphic properties are uncommon to spiropyran-containing LC molecules. Among the compounds investigated, **1a** was found to exhibit a monotropic SmC phase between 90 and 79°C.

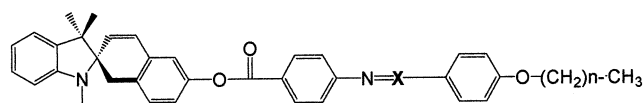
1. Introduction

Thermo- and photo-chromic indolinbenzospiropyran dyes have recently become important in connection with the rapid development of information recording systems, high density optical data storage, displays, holographic devices and as optical switches [2, 3].

Spiropyran (SP) is inherently a chiral compound that undergoes a reversible photochemical ring-opening to give an 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 [4–8]. Photochromic SP liquid crystal materials thus hold considerable potential as candidates for photo-resolvable dopants in UV-transparent nematic and polymeric nematic liquid crystal phases [9, 10]. Chiral liquid crystals that contain an asymmetric carbon 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) [11, 12].

In this connection, we have recently extended our research into various mesogens incorporating a spiro-pyranyl group; these LC molecules are expected to have the chiroptical properties essential for liquid crystal optical switching. We previously reported the synthesis and mesomorphic properties of LC molecules

2a–c containing a diazo styrylated spiropyranyl groups [13]. In this report we describe the study of new liquid crystalline compounds containing a monoazo styrylated indolinbenzospiropyran, **1a–d**, comparing their mesomorphic properties with those of the diazo analogues.



SP-APIB; X = CH (**1a**; n=4, **1b**; n=6, **1c**; n=8, **1d**; n=9)
SP-APAB; X = N (**2a**; n=4, **2b**; n=6, **2c**; n=8, **2d**; n=9)

2. Experimental

2.1. Characterization

Melting points were determined using a Fischer–Jones melting point apparatus and are uncorrected. ¹H NMR spectra are obtained in *DMSO-d*₆ 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 by the Basic Science Research Institute of Korea University at Seoul Campus. DSC thermograms of the compounds were obtained using a DuPont 910 thermal analyser calibrated with indium under N₂ atmosphere at a heating/cooling rate of 5°C min⁻¹. The optical textures and thermal transitions were obtained

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using a Nikon Labophot-2 polarizing microscope equipped with a Mettler FP82HT hot stage. X-ray analyses were carried out at the Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM) of Université Laval using a Rigaku Rotaflex RU-200BH rotating anode, with Ni-filtered CuK α radiation, operating at 55 kV/190 mA. Wide angle and small angle profiles were recorded using Rigaku scillation counters coupled to pulse-height analysers.

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. The alkoxybenzaldehydes **3** were prepared by the procedure of Gray *et al.* [14]. 6-Hydroxy-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] was prepared by condensation of 2-methylene-1,3,3-trimethylindoline (Fischer's base) with 2,5-dihydroxybenzaldehyde, using the procedure of Keum *et al.* [4].

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

The following procedure is representative. To a solution of 4-(4'-pentyloxyphenylimino)benzoic acid **4a** (1 g, 3.2 mmol) and 6-hydroxy-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] **5** (0.94 g, 3.2 mmol) in 100 ml of methylene, were added *N,N'*-dicyclohexylcarbodiimide (DCC, 0.73 g, 3.5 mmol) and 4-dimethylaminopyridine (DMAP, 0.04 g, 0.3 mmol). 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 (EtOAc 5% hexane 95%, v/v). Recrystallization from acetone gave the product **1a**.

2.3.1. 1',3',3'-Trimethylspiro[2H-1-benzopyran-2,2'-indoline]-6-yl 4-(4'-pentyloxyphenylimino)benzoate **1a**

M.p. 125°C, yield 35%. ¹H NMR (300 MHz, CDCl₃): 0.95 (t, 3H), 1.18 (s, 3H), 1.33 (s, 3H), 1.26–1.56 (m, 4H), 1.83 (m, 2H), 2.75 (s, 3H), 4.04 (t, 2H), 5.73 (d, 1H), 6.54 (d, 1H), 6.75 (d, 1H), 6.83 (d, 1H), 6.85 (t, 1H), 6.92 (s, 1H), 6.93 (d, 1H), 6.99 (d, 2H), 7.08 (d, 1H), 7.19 (t, 1H), 7.24 (d, 2H), 7.86 (d, 2H), 8.20 (d, 2H), (8.38 (s, 1H). MS: *m/z* 586(M⁺, 12), 292(100), 223(35), 132(42). High resolution MS: calculated for C₃₈H₃₈N₂O₄ 586.2832; found 586.2835. Anal: calcd C 77.79, H 6.53, N 4.77; found C 77.80, H 6.55, N 4.78%.

2.3.2. 1',3',3'-Trimethylspiro[2H-1-benzopyran-2,2'-indoline]-6-yl 4-(4'-heptyloxyphenylimino)benzoate **1b**

M.p. 116°C, yield 32%. ¹H NMR (300 MHz, CDCl₃): 0.90 (t, 3H), 1.18 (s, 3H), 1.33 (s, 3H), 1.28–1.55 (m, 8H), 1.82 (m, 2H), 2.75 (s, 3H), 4.03 (t, 2H), 5.74 (d, 1H), 6.54 (d, 1H), 6.75 (d, 1H), 6.83 (d, 1H), 6.85 (t, 1H), 6.92 (s, 1H), 6.93 (d, 1H), 6.99 (d, 2H), 7.09 (d, 1H), 7.19 (t, 1H), 7.24 (d, 2H), 7.86 (d, 2H), 8.19 (d, 2H), (8.38 (s, 1H). MS: *m/z* 614(M⁺, 11), 292(100), 223(22), 132(30). High resolution MS: calculated for C₄₀H₄₂N₂O₄ 614.3145; found 614.3147. Anal: calcd C 78.15, H 6.89, N 4.56; found C 78.17, H 6.91, N 4.54%.

2.3.3. 1',3',3'-Trimethylspiro[2H-1-benzopyran-2,2'-indoline]-6-yl 4-(4'-nonyloxyphenylimino)benzoate **1c**

M.p. 102°C, yield 27%. ¹H NMR (300 MHz, CDCl₃): 0.89 (t, 3H), 1.18 (s, 3H), 1.33 (s, 3H), 1.28–1.55 (m, 12H), 1.82 (m, 2H), 2.75 (s, 3H), 4.04 (t, 2H), 5.74 (d, 1H), 6.55 (d, 1H), 6.75 (d, 1H), 6.83 (d, 1H), 6.85 (t, 1H), 6.92 (s, 1H), 6.93 (d, 1H), 6.96 (d, 2H), 7.09 (d, 1H), 7.20 (t, 1H), 7.25 (d, 2H), 7.85 (d, 2H), 8.20 (d, 2H), (8.38 (s, 1H). MS: *m/z* 642(M⁺, 20), 292(100), 223(32), 132(50). High resolution MS: calculated for C₄₂H₄₆N₂O₄ 642.3458; found 642.3460. Anal: calcd C 78.47, H 7.21, N 4.36; found: C 78.46, H 7.22, N 4.37%.

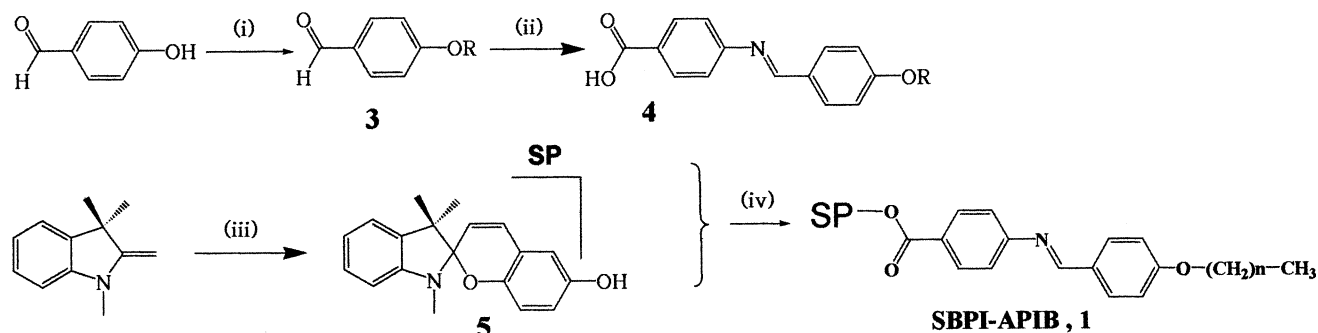
2.3.4. 1',3',3'-Trimethylspiro[2H-1-benzopyran-2,2'-indoline]-6-yl 4-(4'-decanyloxyphenylimino)benzoate **1d**

M.p. 101°C, yield 26%. ¹H NMR (300 MHz, CDCl₃): 0.89 (t, 3H), 1.18 (s, 3H), 1.34 (s, 3H), 1.27–1.56 (m, 14H), 1.83 (m, 2H), 2.75 (s, 3H), 4.04 (t, 2H), 5.74 (d, 1H), 6.54 (d, 1H), 6.76 (d, 1H), 6.83 (d, 1H), 6.86 (t, 1H), 6.92 (s, 1H), 6.93 (d, 1H), 7.00 (d, 2H), 7.09 (d, 1H), 7.19 (t, 1H), 7.25 (d, 2H), 7.86 (d, 2H), 8.20 (d, 2H), (8.38 (s, 1H). MS: *m/z* 656(M⁺, 10), 292(100), 223(28), 132(42). High resolution MS: calculated for C₄₃H₄₈N₂O₄ 656.3614; found 656.3615. Anal: calcd C 78.63, H 7.37, N 4.26; found C 78.66, H 7.38, N 4.27%.

3. Results and discussion

3.1. Synthesis

The aryliminobenzoates **1a–d** were synthesized in 26–35% yield via DCC esterification of 6-hydroxy-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline] **5** with the corresponding 4'-alkoxyphenylimino-4-benzoic acid **4**, as shown in the scheme. The hydroxyspiropyran **5** was readily obtained by reaction of 2,5-dihydroxybenzaldehyde with 2-methylene-1,3,3-trimethylindoline (FB).



Scheme. Synthesis of compounds 1a-d.

3.2. Mesophase characterization

The characterization of liquid crystal phases exhibited by the spiropyranlated arylimino derivatives was achieved primarily by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The benzoates **1a** and **1d** formed monotropic mesophases, whereas **1b** and **1c** formed enantiotropic mesophases, which is quite unusual to the spiropyranlated LC molecules; none of the spiropyranlated LC molecules reported so far formed an enantiotropic mesophase. All the compounds examined formed nematic phases during cooling, and on heating, if enantiomeric (see the table). These are indicated by the schlieren textures observed by POM (figure 1). On cooling, all the compounds except **1c** formed a SmA phase, whereas

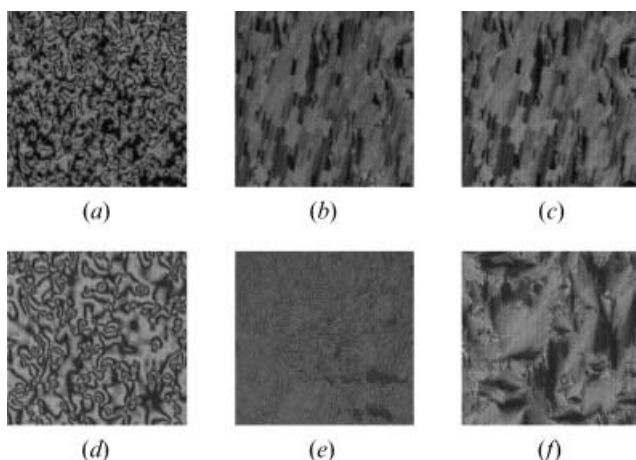


Figure 1. Optical textures of **1a** observed between crossed polarizers on cooling: (a) nematic phase at 119°C, (b) SmA phase at 103.8°C, (c) SmC phase at 90°C; and **1b** (d) nematic phase at 109.6°C, (e) finger-print phase at 91°C, (f) SmA phase at 87.8°C.

only **1b** showed a SmA phase on heating. Surprisingly, **1b** at 91°C on cooling formed a finger-print phase which is generally known behaviour for a chiral nematic phase [15, 16].

The DSC thermogram obtained for **1a** revealed a second order phase transition at 90°C corresponding to the appearance of a SmC phase (figure 2). Examination of compound **1c** by DSC and POM indicated the formation of an enantiotropic nematic phase. The two

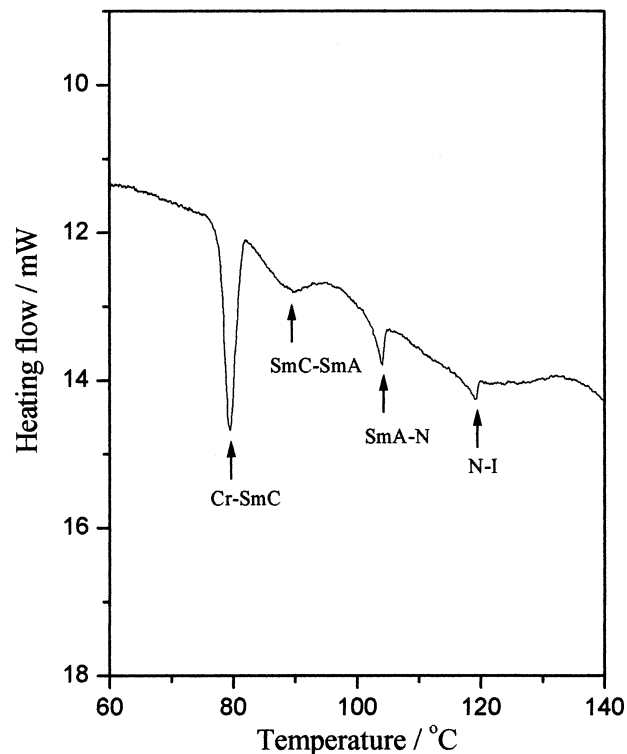


Figure 2. DSC thermogram of **1a** on cooling from isotropic liquid.

Table. Phase transition temperatures of **1a–d** on cooling and heating (°C).

| Compound | on cooling | | | | on heating | | | | |
|--------------------------------|------------|-----|-----|-----|------------|-----|-----|----|-----|
| | I | N | SmA | SmC | Cr | SmA | N | I | |
| SP-APIB, 1a | ● | 119 | ● | 104 | ● | 90 | ● | 79 | ● |
| SP-APIB, 1b | ● | 114 | ● | 91 | ● | | 60 | ● | 101 |
| SP-APIB, 1c | ● | 101 | ● | | ● | | 57 | ● | 95 |
| SP-APIB, 1d | ● | 99 | ● | 90 | ● | | 64 | ● | |
| SP-APAB, 2a^a | ● | 128 | ● | 117 | ● | | 103 | ● | |
| SP-APAB, 2b^a | ● | 113 | ● | 100 | ● | 99 | ● | 95 | ● |
| SP-APAB, 2c^a | ● | 118 | ● | 105 | ● | | 62 | ● | |
| SP-APAB, 2d^a | ● | 111 | ● | 100 | ● | | 92 | ● | |

^aData from reference [5].

series of spiropyranlated LC molecules **1a–d** and **2a–d** showed very similar mesophase behaviour. The monoazo aryliminobenzoates (series **1**) showed lower phase transition temperature ranges than the diazo analogues (series **2**), as shown in the table. Two of the monoazo aryliminobenzoates (**1b** and **1c**) showed enantiotropic mesophase transitions, whereas the diazo analogues showed only monotropic behaviour.

Examination of the compounds by X-ray diffraction (WAXS) showed a wide angle halo and a single sharp diffraction peak at small angle, which is consistent with a SmA phase. At small angle (SAXS), compound **1a** gave a single diffraction peak at a Bragg angle of 2.6° at 85°C, which corresponds to a SmA layer spacing of 33.37 Å. This matches the molecular length of **1a** in its most extended form (33.4 Å, MM2), and rules out the formation of both ring-opened merocyanine forms and dimeric aggregates in the SmA phase region. We were unable to obtain X-ray diffraction data for the SmC phase of **1a** due to its tendency to crystallize in the glass capillary tube below 85°C. Upon further cooling, all the compounds became amorphous solids that slowly crystallized at room temperature.

4. Conclusions

A series of novel liquid crystals, monoazo styrylated benzoates, incorporating a non-activated spiropyran moiety, have been synthesized. Among the compounds investigated, compound **1a** was found to exhibit a monotropic SmC phase, which was our target in the development of photostable spiropyran-containing SmC mesogens. This work has thus shown that it is possible to incorporate a non-activated spiropyran into a SmC mesogen. Another interesting point is that it is the first example of a spiropyran-containing enantiotropic liquid crystal, to the best of our knowledge.

Further work aimed at developing photostable spiropyran-containing SmC mesogens is in progress.

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References

- [1] KEUM, S.-R., CHO, C.-H., and CHOI, Y.-K., 2003, *Dyes and Pigments*, **60**, 147.
- [2] BROWN, G. H. (Editor), 1971, *Photochromism* (New York: Wiley).
- [3] DURR, H., and BOUAS-LAURENT, H. (Editors), 1990, *Photochromism-Molecules and Systems* (Amsterdam: Elsevier).
- [4] KEUM, S.-R., LEE, K. B., KAZMAIER, P. M., and BUNCEL, E., 1994, *Tetrahedron Lett.*, **37**, 1105.
- [5] SWANBURG, S., CHOI, Y.-K., KEUM, S.-R., BUNCL, E., and LEMIEUX, R. P., 1998, *Liq. Cryst.*, **24**, 341.
- [6] KEUM, S.-R., and JANG, H. R., 2003, *Dyes and Pigments*, **57**, 1.
- [7] YITZCHAIK, S., CABRERA, I., BUCHHOLTZ, F., and KRONGAUZ, V., 1990, *Macromolecules*, **23**, 707.
- [8] NATARAJAN, L. V., BUNNING, T. J., and KIM, S. Y., 1994, *Macromolecules*, **27**, 7248.
- [9] RAU, H., 1983, *Chem. Rev.*, **83**, 535.
- [10] HATTORI, U., and URYU, T., 1999, *Liq. Cryst.*, **26**, 1085.
- [11] ZHANG, Y., and SCHUSTER, G. B., 1994, *J. org. Chem.*, **59**, 1855.
- [12] LEMIEUX, R. P., and SCHUSTER, G. B., 1993, *J. org. Chem.*, **58**, 100.
- [13] KEUM, S.-R., LEE, M.-J., and SHIN, S.-T., 2001, *Liq. Cryst.*, **28**, 1587.
- [14] GRAY, G. W., HARTLEY, J. B., and JONES, B., 1995, *J. chem. Soc.*, 1412.
- [15] GRAY, G. W., and GOODBY, J. W. G., 1984, *Smectic Liquid Crystals* (London: Leonard Hill).
- [16] DEMUS, D., and RICHTER, L. (Editors), 1978, *Textures of Liquid Crystals* (New York, Weinheim: VCH).