Fibers and Polymers 2001, Vol.2, No.3, 117-121

Synthesis of Liquid Crystalline Spiroxazine Derivatives

Jian-Zhong Cui, Jae-Ho Kim[1], and Sung-Hoon Kim*

Department of Dyeing and Finishing, College of Engineering, Kyungpook National University, Taegu 702-701, Korea
[1]Department of Molecular Science and Technology, Ajou University, Suwon 442-749, Korea
(Received July 2, 2001; Revised July 30, 2001; Accepted August 6, 2001)

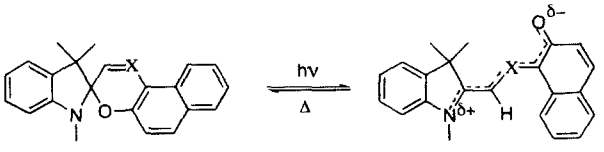
Abstract: Liquid crystalline spiroxazine derivatives have been synthesized. The spiroxazines obtained were characterized by ^{1}H-NMR, IR spectroscopy, UV and GC-MS.

Keywords: Liquid crystalline, Spiroxazine, Photochromism, Mesophase

Introduction

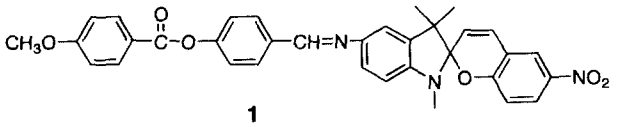
Originally the term photochromism was applied to light-induced, reversible photochemical reactions, which resulted in a visible colour change. However, this definition has been extended to cover reversible transformations between two states with differing absorption spectra, which may be in the UV, visible or IR regions of the electromagnetic spectrum. The transformation is induced in at least one direction by the absorption of electromagnetic radiation and, in the other directions, by spontaneous or thermal reaction. Photochromic spiro compounds are promising objects of research[1,2], since reversible isomerization into a merocyanine dye holds the prospect of usage in optical devices including storage and switches.

Although photochromic compounds have attracted significant attention because of their potential use as sunlight-activated, self-coloured glasses and optical memory media, they still await major commercial exploitation. One of the prime reasons for the lack of industrial applications for photochromic materials, particularly organic photochromic compounds, is their poor durability. Although the photochromism of spiropyran has been extensively studied[3,4], only little work has been carried out on spiroxazine dyes. These two classes of compounds are similar in many aspects, but the replacement of the benzopyran ring by a naphthoxazine ring, which results in spironaphthoxazine, greatly improved resistance to prolonged UV irradiation, which confers greater commercial importance[5].

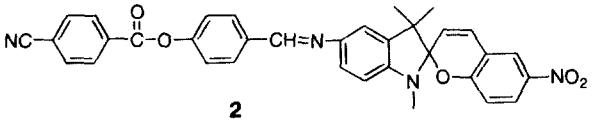


We have previously reported on the synthesis, spectral properties, and solvatochromic properties of spiroxazines[6-8]. We have also reported the preparation and surface properties of spiroxazine monolayer on gold[9-11].

The combination of photochromic and liquid crystalline properties in one molecule may lead to very versatile materials, sensitive to light, and electric and magnetic fields. Attempts to synthesize low molar mass molecules containing both spiropyran and mesogenic groups resulted in formation of a material, giving a thermochromic mesophase (quasi-liquid crystals), which, however, does not exhibit photochromism [12,13]. Compounds **1** and **2** represent examples of such combined molecules. These compounds form a metastable mesophase, which can be aligned in an electrostatic field and stabilized by supercooling to room temperature.

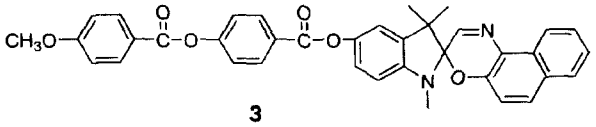


1

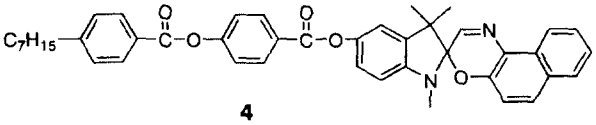


2

The unimolecular thermal isomerization of a photomerocyanine to an indolinospirobenzopyran has been studied in the isotropic and smectic liquid crystalline phases of n-butyl stearate[14]. Spiroxazine molecules **3** and **4** represent quasi-liquid-crystals that show the photochromic effect[15]. The supercooled films of these compounds form blue merocyanine molecules on UV irradiation, which are spontaneously converted back to a noncoloured spiroxazine form in the dark.



3



4

*Corresponding author: shokim@bh.knu.ac.kr

In the present paper, we describe the synthesis and characterization of photochromic liquid crystalline spiroxazine derivatives substituted with a mesogenic group in naphthalene ring.

Experimental

Melting points were determined using an Electrothermal IA 900 apparatus and were uncorrected. Elemental analyses were recorded on a Carlo Elba Model 1106 analyzer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer using electron energy of 70 eV and the direct probe EI method. ^{1}H-NMR spectra were recorded on a Varian Unity Inova 400 MHz FT-NMR spectrometer with TMS as internal standard. UV-visible spectra were recorded on a Shimadzu 2100 spectrometer.

Materials

4'-octyloxy-4-biphenylcarboxylic acid, 4-octyloxybenzoic acid, 4-hexyloxybenzoic acid, 4-pentyloxybenzoic acid, 4-butoxybenzoic acid, 4-octylbenzoic acid, 4-hexylbenzoyl chloride, 4-butylbenzoyl chloride, 1,3-dicyclohexyl-carbodiimide, and 4-dimethylaminopyridine were purchased from Aldrich Chemical Company. 1,3,3-trimethyl-2-methylene-indoline (Fischer's base), 2,7-dihydroxy-naphthalene, and thionyl chloride were purchased from Fluka Chemical Company. 6-bromohexanol was purchased from Sigma Chemical Company. All chemicals were of the highest grade available and were used without further purification.

Synthesis of 1,3,3-trimethyl-6'-hydroxyspiro[2H]-indol-2,3'-[3H]-naphth[2,1-b][1,4] oxazine 5

1,3,3-trimethyl-6'-hydroxyspiro[2H]-indol-2,3'-[3H]-naphth [2,1-b][1,4] oxazine **5** was prepared from 1,3,3-trimethyl-2-methylene-indoline and 1-nitroso-2,7-dihydroxynaphthalene according to the method described in reference[16,17]. Yield 17.0 g (50%), mp. 211.5-214°C. Elemental analysis: C; 76.89, H; 4.97, N; 8.59%. $C_{22}H_{20}N_2O_2$ requires: C; 76.72, H; 5.85, N; 8.13%.

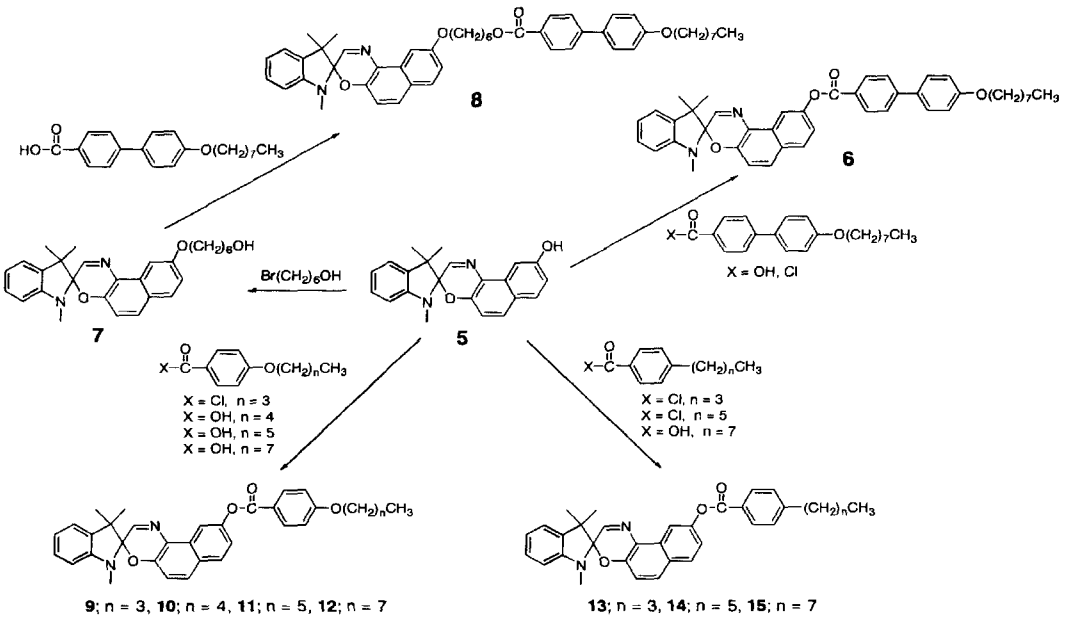
Synthesis of Spiroxazine 6

Method A

0.0015 mole (0.30 g) of compound **5**, 4'-octyloxy-4-biphenylcarboxylic acid, 1,3-dicyclohexylcarbodiimide and 4-dimethylaminopyridine were added into a solution of 80 m*l* methyl dichloride. The solution was refluxed for several hours under nitrogen. After reflux, 120 m*l* methyl dichloride was added into the reaction solution. The mixture was cooled at room temperature and filtered to remove the precipitate. The solvent was removed from filtrate and a solid product obtained was separated by column chromatography with the mixture of hexane and ethyl acetate in 3:1 (v/v) as eluent and recrystallized with hexane/ethyl acetate and ethyl acetate/acetone for two times. Purified compound was white powder. Yield 0.55 g (60%).

Method B

4'-octyloxy-4-biphenylcarboxylic acid (1.63 g, 0.005 mole) and thionyl chloride (1.2 g, 0.010 mole) were reacted for three hours at refluxing temperature. The excessive thionyl chloride was removed by distillation under reduced pressure. 4'-octyloxy-4-biphenylcarbonyl chloride obtained was dissolved in 30 m*l* tetrahydrofuran and followed by dropping into the solution of compound **5** (1.7 g, 0.005 mole) in 30 m*l*



Scheme 1.

tetrahydrofuran containing 0.50 g (0.005 mole) triethylamine during stirring and cooling below 0°C with an ice bath. After addition, the solution was continuously stirred for 2 hours in the ice bath and several hours at room temperature, and then filtered to remove solid product which was triethylamine salt of hydrochloride. Filtrate was evaporated under reduced pressure. Product obtained was washed with ethanol for several times and recrystallized with a mixture of acetone and ethanol. Yield 2.5 g (76%), mp. 159-162°C.

Synthesis of Spiroxazine 7

Compound **5** (6.9 g 0.010 mole), 6-bromohexanol (5.5 g, 0.013 mole), and potassium carbonate (2.0 g) were stirred in methyl alcohol at refluxing temperature. After cooled, white solid obtained was filtered, washed, and recrystallized with methyl alcohol. Yield 4.5 g (50%).

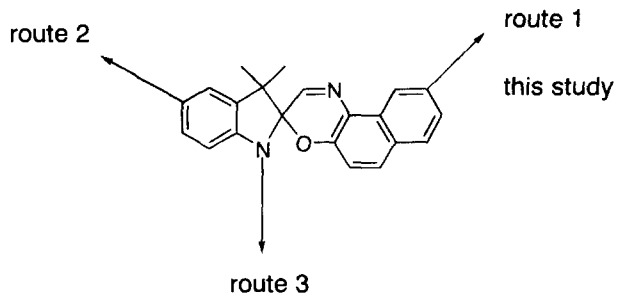
Syntheses of Spiroxazines 8-15

Spiroxazines **8**, **10**, **11**, **12**, and **15** were synthesized according to the method A described above. Spiroxazines **9**, **13**, and **14** were synthesized according to the method B mentioned above.

Results and Discussion

Synthesis of Liquid Crystalline Spiroxazines

An interesting point in photochromic liquid crystals is how the changes of mesophase can be caused by the reversible transformations of the molecular structure of photochromic compounds. These phenomena have been attracting practical interests because photochromism induces reversible changes in various optical properties of liquid crystalline phase and is applicable to optical recording as well as display devices. Generally, there are three ways to modify the chemical structure for liquid crystalline spiroxazine containing mesogenic group. In order to synthesize the liquid crystalline spiroxazine derivatives in this work, the authors choose the route 1 in Scheme 2. Preparation method B gives higher yield than method A. The results are summarized in Table 1. X-ray structural analyses of these compounds are under investigation and will be reported separately.



Scheme 2.

Table 1. Characterization data for the spiroxazines

Compound	MP (°C)	Yield (%)	MS (M^+)	Elemental analysis[c] C	H	N
6	159-160	60[a], 76[b]	652	79.09,	6.87,	4.16
				(79.11;	6.79;	4.29)
7	146-149	50	444	76.20,	7.50,	6.12
				(75.65;	7.26;	6.30)
8	104-109	50[a]	752	78.16,	7.64,	3.62
				(78.16;	7.50;	3.72)
9	156-159	93[b]	520	75.70,	6.56,	5.14
				(76.13;	6.20;	5.38)
10	160-162	40[a]	534	76.13,	6.51,	5.15
				(76.38;	6.41;	5.24)
11	145-146	40[a]	548	76.61,	6.81,	4.94
				(76.62;	6.61;	5.11)
12	90-94	45[a]	576	76.95,	7.20,	4.76
				(77.06;	6.99;	4.86)
13	137-139	75[b]	504	78.78,	6.26,	5.37
				(78.55;	6.39;	5.55)
14	143-144	70[b]	532	78.64,	6.98,	5.05
				(78.92;	6.81;	5.26)
15	106-108	40[a]	560	79.17,	7.41,	4.87
				(79.25;	7.19;	5.00)

[a]method A; [b]method B; [c]calculated values are given in parentheses.

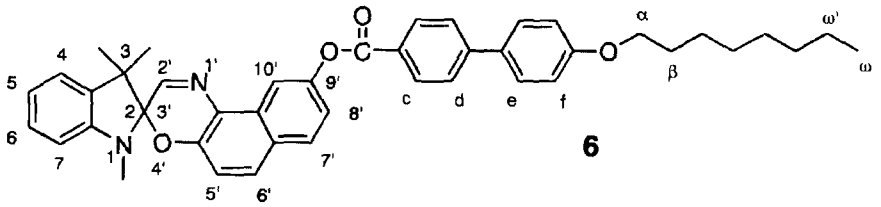
Spectroscopic Properties of Liquid Crystalline Spiroxazines 6, 8-15

Spiroxazines formed colored merocyanine form with UV-

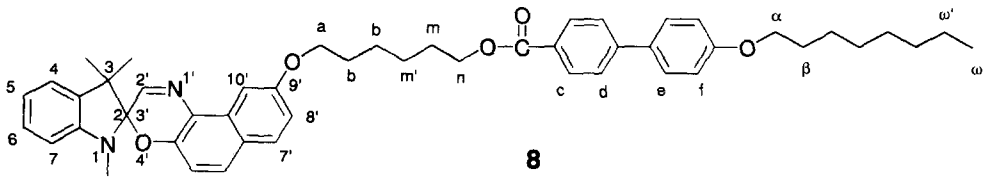
Table 2. IR spectroscopy data for compounds **6**, **8-15**

Compound	Frequencies (cm^{-1})
6	3053(w), 2956(m), 2926(s), 2875(s), 2854(m), 1739(s), 1607(s), 1250(s), 1067(s)
8	3058(w), 2931(s), 2859(s), 2814(m), 1719(s), 1607(s), 1281(s), 1250(s), 833(s)
9	3053(w), 2956(m), 2931(s), 2870(m), 2813(w), 1739(s), 1612(s), 1485(s), 1250(s)
10	3058(w), 2966(s), 2931(s), 2875(m), 2854(m), 1739(s), 1607(s), 1250(s), 1169(s)
11	3053(w), 2956(s), 2931(s), 2880(m), 2859(m), 1739(s), 1612(s), 1515(s), 1250(s)
12	3053(w), 2875(m), 2956(m), 2931(s), 2859(m), 2814(w), 1739(s), 1612(s), 1250(s)
13	3063(w), 2961(s), 2931(s), 2875(m), 2859(m), 2814(w), 1739(s), 1612(s), 1250(s)
14	3063(w), 2961(s), 2931(s), 2859(m), 1740(s), 1617(s), 1490(s), 1250(s), 1021(s)
15	3063(w), 2961(s), 2931(s), 2859(m), 1740(s), 1612(s), 1490(s), 1250(s), 1064(s)

The symbols denoted as follows: s= strong and sharp, m=medium, w=weak.



6



8

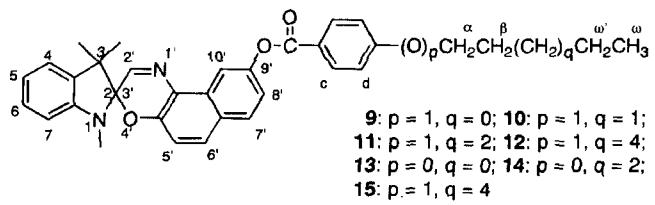
light radiation, and the colored merocyanine forms have a very short life time. However, the substituents (mesogenic group) did not seem to affect the λ_{max} of spiroxzines very much.

Table 2 summarized the IR spectral frequencies of synthesized spiroxazines. The C-H stretching vibrations were observed at 2966-2813 cm^{-1}, and these compounds also showed characteristic carbonyl absorptions at 1719-1740 cm^{-1}.

^{1}H-NMR spectral data of the spiroxazines are also discussed. From ^{1}H-NMR spectra, different chemical shifts between hydrogen atoms H(3a) and H(3b) in methyl groups bonded to carbon atom C(3) were observed in spiroxazines (**6**, **9**, **10**, **12**), because C(3) was bonded to a chiral carbon C(2). Oxygen atom O(4') bonded to C(2) affects electron density of the hydrogen atoms by space effects. Electron density of the hydrogen atoms in the same side with oxygen atom O(4') was different from the others, The difference of chemical shifts between hydrogen atoms H(3a) and H(3b) in the two methyl groups was about 0.003-0.007 ppm.

Compound **6** ^{1}H-NMR (CD_3COCD_3): 0.72 (3H, t, H(ω)), 1.11-1.22 (8H, m), 1.175 (3H, s, H(3)), 1.183 (3H, s, H(3)), 1.33 (2H, m, H(ω')), 1.64 (2H, m, H(β)), 2.61 (3H, s, H(1)), 3.90 (2H, t, H(α)), 6.48 (1H, d, J=7.7 Hz, H(7')), 6.69 (1H, t, H(5')), 6.69 (2H, d, J=8.9 Hz, H(f)), 6.91 (1H, d, J=8.9 Hz), 7.00 (2H, m), 7.26 (1H, m), 7.57 (3H), 7.66 (1H, s, H(2')), 7.71 (2H, m), 7.78 (1H, d), 8.13 (2H, d, H(c)), 8.24 (1H, d, H(10')).

Compound **8** ^{1}H-NMR ($CDCl_3$): 0.89 (3H, t, H(ω)), 1.30-1.32 (8H, m), 1.34 (6H, s, H(3)), 1.46 (2H, m, H(ω')), 1.61 (4H, m, H(b'), H(m')), 1.82 (4H, m, H(b), H(β)), 1.93 (2H,



9: p = 1, q = 0; **10**: p = 1, q = 1;
11: p = 1, q = 2; **12**: p = 1, q = 4;
13: p = 0, q = 0; **14**: p = 0, q = 2;
15: p = 1, q = 4

m), 2.78 (3H, s, H(1)), 4.00 (2H, t, H(α)), 4.20 (2H, t, H(a)), 4.37 (2H, t, H(n)), 6.57 (1H, d, H(7')), 6.84 (1H, d, H(5')), 6.89 (1H, t), 6.97 (2H, d, J=8.7 Hz), 7.03 (1H, d), 7.07 (1H, d), 7.22 (1H, d), 7.53 (2H, d, J=8.7 Hz, H(e)), 7.55 (1H), 7.59 (2H, d, J=8.3 Hz, H(d)), 7.63 (1H, d, J=8.9 Hz), 7.71 (1H, s, H(2')), 7.85 (1H, s, H(10')), 8.07 (2H, d, J=8.3 Hz, H(c)).

Compound **9** ^{1}H-NMR ($CDCl_3$): 1.01 (3H, t, H(ω)), 1.348 (3H, s, H(3)), 1.352 (3H, s, H(ω)), 1.54 (2H, m, H(ω')), 1.83 (2H, m, H(β)), 2.77 3H, s, H(1)), 4.07 (2H, t, J=6.5 Hz, H(α)), 6.58 (1H, d, J=7.8 Hz, H(7')), 6.90 (1H, t, H(5')), 6.99 (3H), 7.09 (1H, d, J=7.1 Hz), 7.22 (1H, m), 7.26 (1H, m), 7.62 (1H, d, J=8.8), 7.71 (1H, s, H(2)), 7.79 (1H, d, J= 8.8 Hz), 8.19 (2H, d, J=8.8 Hz, H(c)), 8.35 (1H, d, J=2.2 Hz, H(10')).

Compound **10** ^{1}H-NMR ($CDCl_3$): 0.96 (3H, t, H(ω)), 1.347 (3H, s, H(3)), 1.352 (3H, s, H(3)), 1.41-1.48 (4H, m), 1.84 (2H, q, J=7.3 Hz, H(β)), 2.76 (3H, s, H(1)), 4.06 (2H, t, H(α)), 6.58 (1H, d, H(7')), 6.90 (1H, t, H(5')), 6.99 (2H, d, H(d)), 7.00 (1H), 7.08 (1H, d), 7.21 (1H), 7.28 (1H), 7.67 (1H, d, J=8.9 Hz), 7.71 (1H, s, H(2')), 7.79 (1H, d, J=8.8 Hz), 8.20 (2H, d, J=8.9 Hz, H(c)), 8.36 (1H, d, H(10')).

Compound **11** ^{1}H-NMR ($CDCl_3$): 0.93 (3H, t, J=7.0 Hz, H(ω)), 1.35-1.39 (10H, m), 1.50 (2H, m, J=7.2 Hz, H(ω')), 1.84 (2H, q, J=6.6 Hz, H(β)), 2.77 (3H, s, H(1)), 4.06 (2H, t, J=6.6 Hz, H(α)), 6.58 (1H, d, J=7.7 Hz, H(7')), 6.89 (1H, t, H(5')), 6.99 (3H, m), 7.08 (1H, d), 7.22-7.27 (2H, m), 7.67 1H, d, J=8.9 Hz), 7.71 (1H, s, H(2')), 7.79 (1H, d, J=8.8 Hz), 8.19 (2H, d, J=8.8 Hz, H(c)), 8.35 (1H, d, J=2.2 Hz, H(10')).

Compound **12** ^{1}H-NMR ($CDCl_3$): 0.90 (3H, t, H(ω)), 1.31 (8H, m), 1.348 (3H, s, H(3)), 1.352 (3H, s, H(3)), 1.49 (2H, m, H(ω')), 1.84 (2H, m, H(β)), 2.77 (3H, s, H(1)), 4.06 (2H, t, H(α)), 6.58 (1H, d, J=7.7 Hz, H(7')), 6.91 (1H, t, H(5')), 6.98 (1H), 6.99 (2H, d, J=8.8 Hz, H(d)), 7.09 (1H, d, J=7.6), 7.22-7.28 (2H, m), 7.67 (1H, d), 7.71 (1H, s, H(2')), 7.79 (1H, d), 8.19 (2H, d, J=8.7 Hz, H(c)), 8.35 (1H, d, J=2.2 Hz, H(10')).

Compound **13** ^{1}H-NMR ($CDCl_3$): 0.96 (3H, t, J=7.4 Hz, H(ω)), 1.349 (3H, s, H(3)), 1.354 (3H, s, H(3)), 1.39-1.42

(2H, m), 1.66 (2H, m, H(β)), 2.72 (2H, t , H(α)), 2.77 (3H, s, H(1)), 6.58 (1H, d, J=7.9 Hz, H(7')), 6.90 (1H, t, H(5')), 7.00 (1H, d, J=8.9 Hz), 7.10 (1H, d), 7.23 (1H, m), 7.27 (1H, d, J=8.5 Hz), 7.34 (2H, d, J=8.2 Hz, H(d)), 7.67 (1H, d, J=8.9 Hz), 7.71 (1H, s, H(2')), 7.79 (1H, d, J=8.8 Hz), 8.16 (2H, d, J=8.3 Hz, H(c)), 8.37 (1H, d, J=2.4 Hz, H(10')).

Compound **14** ^{1}H-NMR ($CDCl_3$): 0.90 (3H, t, J=6.8 Hz, H(ω)), 1.3-1.38 (12H, m), 1.67 (2H, q, H(β)), 2.72 (2H, t, J= 8.0 Hz, H(α)), 2.77 (3H, s, H(1)), 6.58 (1H, d, J=7.8 Hz, H(7')), 6.90 (1H, t, H(5')), 7.00 (1H, d, J=8.8 Hz), 7.08 (1H, d), 7.22 (1H, m), 7.27 (1H, m), 7.34 (2H, d, J=8.1 Hz, H(d)), 7.67 (1H, d, J=8.9 Hz), 7.71 (1H, s, H(2')), 7.79 (1H, d, J=8.8 Hz), 8.16 (2H, d, J=8.1 Hz, H(c)), 8.37 (1H, d, J=2.1 Hz, H(10')).

Compound **15** ^{1}H-NMR ($CDCl_3$): 0.89 (3H, t, J=6.6 Hz, H(ω)), 1.25-1.35 (16H, m), 1.67 (2H, m, H(β)), 2.71 (2H, H(α)), 2.73 (3H, s, H(1)), 6.58 (1H, d, J=7.8 Hz, H(7')), 6.90 (1H, t, H(5')), 7.00 (1H, d, J=8.9 Hz), 7.08 (1H, d), 7.22 (1H, m), 7.27 (1H, m), 7.34 (2H, d, J=8.0 Hz, H(d)), 7.67 (1H, d, J=8.9 Hz), 7.71 (1H, s, H(2')), 7.79 (1H, d, J=8.8 Hz), 8.16 (2H, d, J=8.0 Hz, H(c)), 8.36 (1H, d, J=1.6 Hz, H(10')).

Low molecular weight liquid crystals and polymer liquid crystals have been widely used as active media in display devices. Our research on the photochromical phase transition behaviors of spiroxazine liquid crystalline systems aims the optical-image storage devices. The liquid crystalline properties of the spiroxazines synthesized in this paper will be reported separately.

Acknowledgements

This work was supported by grant No. 2000-2-30800-001-3 from the Basic Research Program of the Korea Science & Engineering Foundation. This work was supported by the grant Post-Doc. Program, Kyungpook National University (2000).

References

1. G. H. Brown, "Photochromism", John Wiley and Sons Inc., New York, 1991.
2. H. Durr and H. Bonas-Laurent, "Photochromism Molecules and Systems", Elsevier, Amsterdam, 1990.
3. S. Kawauchi, H. Yoshida, N. Yamashita, M. Ohira, S. Saeda, and M. I. Werie, *Bulletin of Chemical Society of Japan*, **63**, 267 (1990).
4. D. A. Reeves and F. Wilkinson, *Journal of Chemical Society, Faraday Transition*, **69**, 1341 (1973).
5. T. Okudahida, *Seni Kakkaishi Japan*, **48**, 253 (1992).
6. S. H. Kim and S. N. Lee, *Chemistry Express*, **7**, 849 (1992).
7. S. H. Kim, L. S. Park, D. J. Kim, K. J. Kil, and S. C. Jung, *Chemistry Express*, **7**, 713 (1993).
8. S. H. Kim, S. J. Park, and K. H. Song, *Chemistry Express*, **8**, 741 (1993).
9. S. H. Kim, S. M. Lee, J. H. Park, J. H. Kim, K. N. Koh, and S. W. Kang, *Dyes and Pigments*, **45**, 55 (2000).
10. S. H. Kim, K. S. Ock, J. H. Im, J. H. Kim, K. N. Koh, and S. W Kang, *Dyes and Pigments*, **46**, 55 (2000).
11. S. H. Kim, K. S. Ock, J. H. Kim, K. N. Koh, and S. W. Kang, *Dyes and Pigments*, **48**, 1 (2000).
12. E. P. Shvartsman and V. A. Krongauz, *Nature*, **309**, 608 (1984).
13. E. P. Shvartsman and V. A. Krongauz, *Journal of Physical Chemistry*, **88**, 6448 (1984).
14. J. P. Otruba and R. G. Weiss, *Mol. Cryst. Liq. Cryst.*, **80**, 165 (1982).
15. L. Shrabina, F. Buchholtz, S. Yitzchaik, and U. A. Krongauz, *Mol. Cryst. Liq. Cryst.*, **7**, 643 (1990).
16. T. Kakishita, K. Matsumoto, T. Kiyotsukuri, K. Matsumura, and M. Hosoda, *J. Hetercyclic Chem.*, **29**, 1709 (1992).
17. H. Dürr, Y. Ma, and G. Corterllaro, *Synthesis*, 294 (1995).