

Synthesis and Photochromic Properties of the Derivatives of Spiroyrans Containing a Mesogenic Group

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Abstract: Two series of novel spiropyran derivatives containing a mesogenic group have been prepared. Their photochromic behaviors were first investigated with the aid of absorption spectral measurements.

Keywords: Photochromic, spiroyrans, liquid crystal.

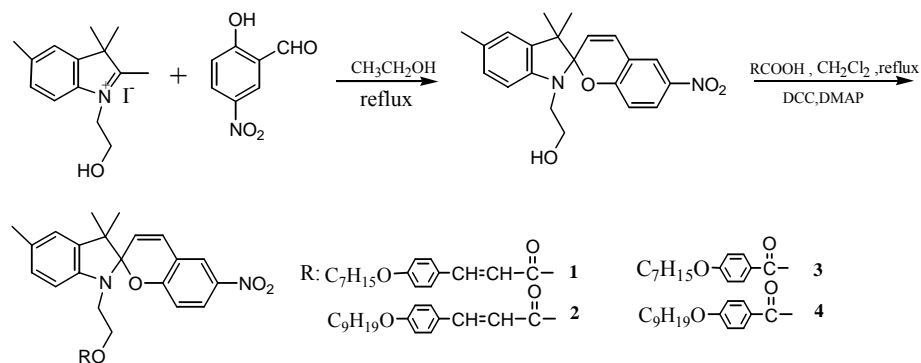
The photochromic compounds continue to attract significant attention in view of their general applicability as optical information storage materials or switching devices¹⁻². In order to develop novel bifunctional and multifunctional materials, special attention has been paid to photochromic liquid crystalline compounds. Many studies have been carried out for all kinds of mixed systems, which are to dope small amounts photochromic compounds into liquid crystal³⁻⁴. However, the combination of the properties of photochromic and liquid crystalline in one molecule is only several examples, which was reported by T. Shrabina⁵ in 1990 and S. H. Kim⁶ in 2003 and G. H. Mehi in 2004⁷⁻⁸. In this report, two series of novel spiropyran derivatives containing a mesogenic group have been prepared. Their photochromic behaviors were first investigated with the aid of absorption spectral measurements.

Results and Discussion

The condensation of 1-(2-hydroxyethyl)-2, 3, 3, 5-tetramethylindoleninium iodide with 5-nitrosalicylaldehyde gave the spiroyrans derivative, which reacts with carboxylic acids with liquid crystal properties by using DCC (N, N'-dicyclohexylcarbodiimide)/DMAP (4-dimethylaminopyrimidine) as the condensation reagent and catalyst, respectively, in dichloromethane to form corresponding spiropyran derivatives **1-4**⁹⁻¹² containing a mesogenic groups (**Scheme 1**). The crude product was purified by silica gel column chromatography using the mixed solvent petroleum ether/ethyl acetate (v:v = 3:1) as the eluent and the yields are about 85-90%.

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Scheme 1



The photochromic properties of the products obtained were investigated simply by their UV-Vis spectra in selected solvent before and after the irradiation of ultraviolet light. The results showed that compounds **1-4** had good photochromic properties in the solutions, which were similar to the spiro photochromic compounds themselves. For example, the absorption of compound **1** in ethanol and dichloromethane in the visible region rise obviously after ultraviolet irradiation (**Figure 1**).

The compound **1-4**, their UV-Vis spectra in selected solvent revealed that absorption varied greatly in the region 400-600 nm before and after irradiation as listed in **Table 1**. There are different photochromic behaviors in different solvents. Red shift enhance in polar solvents. As was shown earlier, it exists in quinonoic form in non-polar solvents and its contribution to the bipolar structure rises slightly with increase in solvent polarity¹³.

The products **1-4** can also turn their color in solid state with the change of temperature. For example, the color of compound **1** is yellow in room temperature and becomes yellow-green, then green, and then blue following the rise of temperature. So the product is not only sensitive to light, but also sensitive to heat. The further research of the liquid crystalline properties by DSC, POM and XRD is being carried out in our lab. And we will report it in elsewhere.

Figure 1 The UV-Vis absorption of **1** in dichloromethane (a) and in ethanol (b)

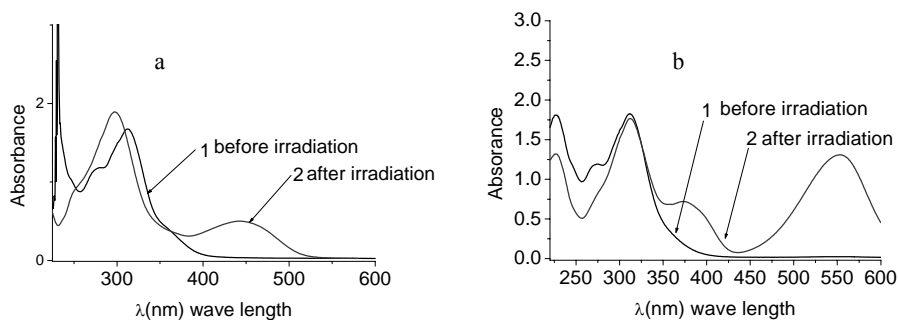


Table 1 The wavelength of maximum absorption of compound **1-4** in the visible region in the different solvents before and after irradiation

Compound	λ max (nm)					
	ethanol		dichloromethane		n-hexane	
	before	after	before	after	before	after
1	none	556	none	445	none	none
2	none	573	none	450	none	none
3	none	576	none	406	none	none
4	none	550	none	452	none	none

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- Data of **1**: ^1H NMR (CDCl_3 , 300 MHz, δ ppm) 0.89 (t, 3H, $J=6.9\text{Hz}$, $-\text{CH}_2\text{CH}_3$), 1.16(m, 6H, $\text{C}(\text{CH}_3)_2$), 1.27-1.45 (m, 8H, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.76 (m, 2H, $-\text{OCH}_2\text{CH}_2-$), 2.33(s, 3H, Ar- CH_3), 3.46 (t, 2H, $J=6.0\text{Hz}$, $\text{NCH}_2\text{CH}_2\text{O}$), 3.98(t, 2H, $J=6.6\text{Hz}$, $-\text{OCH}_2\text{CH}_2-$), 4.33 (t, 2H, $J=6.0\text{Hz}$, $\text{NCH}_2\text{CH}_2\text{O}$), 5.86(d, 1H, $J=10.5\text{Hz}$, $-\text{CH}=\text{CH}-$), 6.14(d, 1H, $J=15.9\text{Hz}$, $-\text{CO OCH}=\text{CH}-$), 6.62 (d, 1H, $J=7.8\text{Hz}$, Ar-H), 6.75(d, 1H, $J=8.7\text{Hz}$, Ar-H), 6.87(d, 2H, $J=8.4\text{Hz}$, Ar-H), 6.90(s, 1H, Ar-H), 6.92(t, 1H, $J=10.2\text{Hz}$, $-\text{CH}=\text{CH}-$), 7.02(d, 1H, $J=7.8\text{Hz}$, Ar-H), 7.41(d, 2H, $J=8.4\text{Hz}$, Ar-H), 7.56(d, 1H, $J=15.9\text{Hz}$, $-\text{COOCH}=\text{CH}-$), 7.99(d, 2H, $J=8.1\text{Hz}$, 2 Ar-H). MS (+cESI): m/z 611.31 (M+1). Anal. Calcd. For $\text{C}_{37}\text{H}_{42}\text{O}_6\text{N}_2$, C: 72.79%, H: 6.89%, N: 4.59%; Found C: 72.64%, H: 6.92%, N: 4.38%.
- Data of **2**: MS (+cESI): m/z 639.29 (M+1). Anal. Calcd. For $\text{C}_{37}\text{H}_{42}\text{O}_6\text{N}_2$, C: 73.33%, H: 7.26%, N: 4.39%; Found C: 73.35%, H: 7.29%, N: 4.28%.
- Data of **3**: ^1H NMR (CDCl_3 , 300 MHz, δ ppm) 0.86 (t, 3H, $J=6.9\text{Hz}$, $-\text{CH}_2\text{CH}_3$), 1.16(m, 6H, $\text{C}(\text{CH}_3)_2$), 1.27-1.46 (m, 8H, $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.75 (m, 2H, $-\text{OCH}_2\text{CH}_2-$), 2.33(s, 3H, Ar- CH_3), 3.58 (t, 2H, $J=6.0\text{Hz}$, $\text{NCH}_2\text{CH}_2\text{O}$), 4.01(t, 2H, $J=6.6\text{Hz}$, $-\text{OCH}_2\text{CH}_2-$), 4.43 (t, 2H, $J=6.0\text{Hz}$, $\text{NCH}_2\text{CH}_2\text{O}$), 5.86(d, 1H, $J=10.5\text{Hz}$, $-\text{CH}=\text{CH}-$), 6.40 (d, 1H, $J=7.8\text{Hz}$, Ar-H), 6.63(d, 1H, $J=8.7\text{Hz}$, Ar-H), 6.72(d, 1H, $J=8.4$), 6.88(d, 1H, $J=8.7\text{Hz}$, Ar-H), 6.92(t, 1H, $J=10.2\text{Hz}$, $-\text{CH}=\text{CH}-$), 7.00(d, 1H, $J=7.8\text{Hz}$, Ar-H), 7.40(d, 1H, $J=8.4\text{Hz}$, Ar-H), 7.89(d, 2H, $J=8.7$ Ar-H), 8.12(d, 2H, $J=8.4\text{Hz}$, 2 Ar-H). MS (+cESI): m/z 585.66 (M+1). Anal. Calcd. For $\text{C}_{37}\text{H}_{42}\text{O}_6\text{N}_2$, C: 71.91%, H: 6.85%, N: 4.79%; Found C: 71.76%, H: 7.22%, N: 4.58%.
- Data of **4**: MS (+cESI): m/z 613.55 (M+1). Anal. Calcd. For $\text{C}_{37}\text{H}_{42}\text{O}_6\text{N}_2$, C: 72.55%, H: 7.19%, N: 4.58%; Found C: 72.27%, H: 7.26%, N: 4.85%.
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