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Synthesis and photochromic properties of spironaphth [1,2-b]oxazine containing a reactive substituent

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Abstract

Spironaphth[1,2-b]oxazines having either an allyl group or a 3-(diethoxymethylsilyl)propyl group on the *N*-atom of the indoline ring have been prepared, as potential substrates for photochromic materials. In addition to displaying the well-known photochromism between the closed and open forms, the present spirooxazines exhibit photochromism between two geometric isomers of the colored open form. This behavior provides the basis for a non-destructive read-out system having light-induced information memory. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Spirooxazine; Photochromism; Non-destructive read-out

1. Introduction

Spironaphth[2,1-b]oxazine **1**, a photostable photochromic compound [1], has been investigated for its potential use in reversible light-induced information memory devices [2]. In this regard, it has been found that a limitation in the utility of dye **1** is its destruction of memory by the associated read-out light. Recently, we found that spironaphth[1,2-b]oxazine **2a** exhibits non-destructive read-out behavior [3]. However, the colored merocyanine structure formed by the photochromic transformation of **2a** is thermally unstable. It is clear that stabilizing the colored form of **2a** is essential to its commercial application.

In other work, we studied the photochromic behavior of a spirobenzopyran bonded covalently to polymeric siloxanes [4–8], and found that the thermal stability of the colored form was improved by a factor of 10^4 when incorporated in a phenylsiloxane resin versus in ethanol solution [4,5]. Since colour loss was accompanied by a significant change in molecular conformation, the enhanced stability may be attributable to a limited free volume in the polymer matrix surrounding the spiropyran.

Two methods for introducing a spirooxazine moiety into siloxane polymers have been reported. As shown in Scheme 1, these methods involve the hydrosilation of an Si–H containing siloxane polymer (**6**) with an allyl-substituted spirooxazine (**4**) [9], and the hydrolysis/polycondensation of ethoxysilanes (**7**) in the presence of the spirooxazine containing an ethoxysilyl group (**5**) [4,7]. In the present study, we conducted the synthesis and evaluation of new photochromic spironaphth[1,2-b] oxazines having non-destructive read-out properties.

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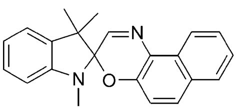

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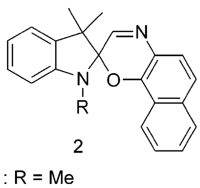
Spironaphth[2,1-b]oxazine



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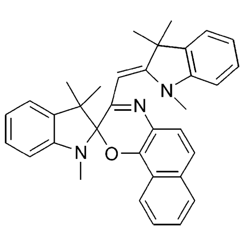
a : R = Me
b : R = $CH_2CH=CH_2$
c : R = $CH_2CH_2CH_2SiMe(OEt)_2$

Spironaphth[1,2-b]oxazine



3

In this regard, spirooxazines suitable for the chemistry reported in Scheme 1 were target compounds.

2. Experimental

2.1. Materials

Unless specified otherwise, commercially available reagents and solvents were used as received. Ethanol was dried over 3 Å molecular sieves and 2-nitroso-naphthol was prepared by a previously reported method [10].

2.2. Measurements

^1H NMR spectra were recorded on a 200 MHz Gemini 2000 spectrometer using TMS or $CHCl_3$ ($\delta = 7.24$) in $CDCl_3$ as the internal standard. EI–MS data were obtained using a Jeol DX302 spectrometer. Measurement of absorption spectra at low temperature was conducted using 1.7×10^{-5} M solutions of **2b** or **2c** in hexane. Visible absorption spectra were recorded on a Shimadzu UV-3100PC spectrophotometer. The temperature of the samples was regulated by an ND1704 Variable Temperature Liquid Nitrogen Criostat (Oxford). UV light and visible light of $\lambda > 500$ nm and $\lambda > 600$ nm were obtained using an UXL-500D Ushio xenon lamp and Toshiba UV-D33S, Y-50, and R-60 filters, respectively.

2.3. Synthesis

2.3.1. Spirooxazine **2b**

A solution of 2,3,3-trimethyl-3H-indole (3.0 g, 19 mmol) and allyl iodide (3.8 g, 23 mmol) in EtOH (100 ml) was stirred under reflux for 3 h. The resultant solid (3.3 g) was collected by filtration and washed with EtOAc. A portion of the solid (1.8 g) was dissolved in NaOH (2M, 15 ml), and the resultant allyl-substituted indoline was extracted into Et_2O. After drying over anhydrous Na_2SO_4, the solvent was evaporated and the residue was dissolved in EtOH (10 ml). To this solution, 2-nitroso-1-naphthol (0.87 g, 5.0 mmol) in EtOH (15 ml) was added. The mixture was stirred under reflux and Ar for 3 h. Following the removal of solvent and column chromatography twice (Merck Silica gel 60, using 9 hexane/1 ethyl acetate), spirooxazine **2b** (34.4 mg, 1.9% based on the nitrosonaphthol) was obtained.

^1H NMR (200 MHz, $CDCl_3$): δ 1.36 (*s*, C-Me, 3H), 1.39 (*s*, C-Me, 3H), 3.83 (*d*, $J = 5.0$ Hz, 1H), 3.90 (*d*, $J = 5.0$ Hz, 1H), 5.07 (*d*, $J = 10.4$ Hz, 1H), 5.21 (*d*, $J = 17.2$ Hz, 1H), 5.84 (*m*, $J = 20.4$ Hz, 1H), 6.63 (*d*, $J = 7.8$ Hz, 1H), 6.92 (*t*, $J = 14.8$ Hz, 1H), 7.11 (*d*, $J = 7.2$ Hz, 1H), 7.20 (*t*, $J = 15.2$ Hz, 1H), 7.36 (*t*, $J = 13.2$ Hz, 1H), 7.42 (*d*, $J = 9.2$ Hz, 1H), 7.45 (*t*, $J = 13.6$ Hz, 1H), 7.53 (*d*, $J = 8.6$ Hz, 1H), 7.70 (*s*, 1H), 7.76 (*d*, $J = 7.2$ Hz, 1H), 8.01 (*d*, $J = 8.0$ Hz, 1H)

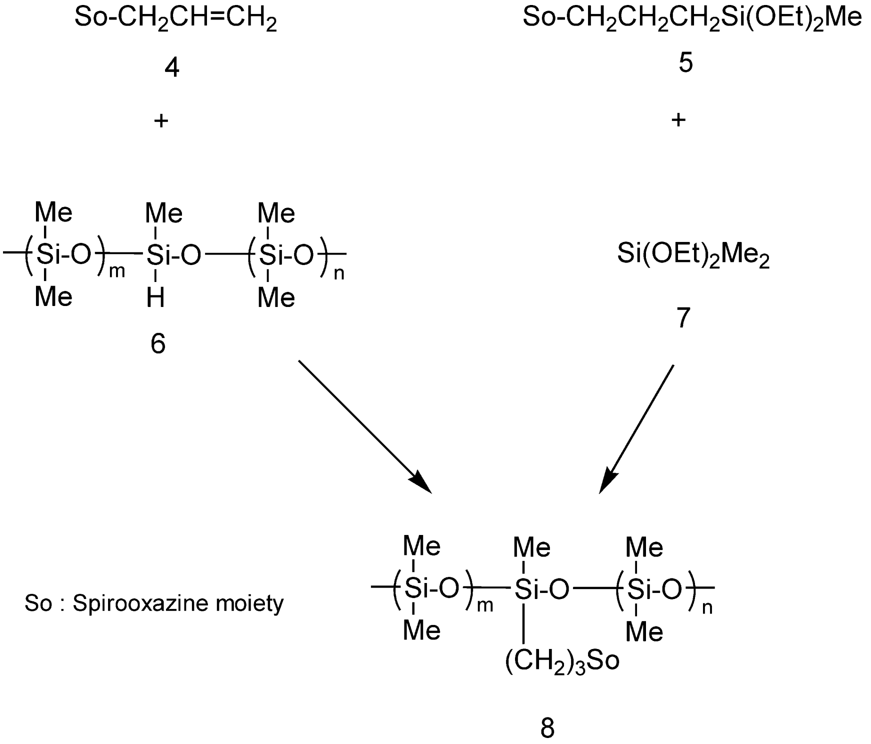
EI–MS (70 eV); *m*/*z* (rel. int.): 354 (M^+, 85%), 339 (100), 327 (20), 313 (7), 297 (20), 269 (30), 185 (67), 144 (85), 115 (58).

2.3.2. Diethoxy(3-iodopropyl)methylsilane

This precursor for the synthesis of dye **2c** was prepared from dimethoxy(3-chloropropyl)methylsilane by ethanolysis and a halogen-substitution reaction with NaI in acetone [7].

2.3.3. Spirooxazine **2c**

A mixture of 2,3,3-trimethyl-3H-indole (0.80 g, 5.0 mmol) and diethoxy(3-iodopropyl)methylsilane



Scheme 1. Approaches to the synthesis of photochromic siloxane polymers.

(1.51 g, 5.0 mmol) was stirred for 3 h at 100 °C under Ar. The reaction mixture was cooled to 25 °C and EtOH (10 ml) was added followed by a solution of Et_3N (0.7 ml) and 2-nitroso-1-naphthol (0.87 g, 5.0 mmol) in EtOH (10 ml). The mixture was stirred at reflux under Ar for 3 h. Thin-layer chromatographic (TLC) analysis of the crude product suggested the formation of two photochromic compounds (R_f~0.13 and 0.22). Following the removal of solvent and column chromatography twice (Merck Silica gel 60, using 9 hexane/1 ethyl acetate), spirooxazine **2c** (18.8 mg, 0.77% based on the indole) was obtained.

^{1}H NMR (200 MHz, $CDCl_3$): δ–0.04 (*s*, 3H), 0.51 (*t*, J= 14.2 Hz, 1H), 0.56 (*t*, J= 13.8 Hz, 1H), 1.05 (*m*, J=24.0 Hz, 2H), 1.11 (*t*, J= 14.0 Hz, 3H), 1.12 (*t*, J= 14.2 Hz, 3H), 1.34 (*s*, 6H), 3.18 (*t*, J= 12.6 Hz, 1H), 3.22 (*t*, J= 13.0 Hz, 1H), 3.63 (*q*, J=20.8 Hz, 2H), 3.65 (*q*, J= 21.0 Hz, 2H), 6.61 (*d*, J=7.6 Hz, 1H), 6.88 (*t*, J= 14.8 Hz, 1H), 7.08 (*d*, J=7.6 Hz, 1H), 7.21 (*t*, J= 15.2 Hz, 1H), 7.35 (*t*, J= 13.6 Hz, 1H), 7.41 (*d*, J=9.0 Hz, 1H), 7.44 (*t*, J= 14.6 Hz, 1H), 7.52 (*d*, J=8.8 Hz, 1H), 7.67 (*s*, 1H), 7.74 (*d*, J= 6.4 Hz, 1H), 8.00 (*d*, J= 8.2 Hz, 1H)

EI–MS (70 eV); *m*/*z* (rel. int.): 488 (M^+, 90%), 473 (7), 427 (20), 388(5), 327 (63), 158 (90), 133 (78), 105 (30), 89 (50), 77 (100), 61 (23).

2.3.4. Compound ***3***

The same procedure used to prepare dye **2c** was employed, using methyl iodide instead of diethoxy(3-iodopropyl)methylsilane. TLC analysis revealed that the crude product was a mixture of compound **3** (R_f~0.16) and spirooxazine **2a**. Chromatography three times on silica gel 60 using 9 hexane/1 ethyl acetate as the eluent gave reasonably pure **3**.

EI–MS (70 eV); *m*/*z* (rel. int.): 499 (M+, 75%), 484 (12), 354 (37), 339 (53), 325 (42), 309 (35), 269 (20), 185 (35), 172 (62), 160 (70), 144 (100), 115 (37), 77 (30).

3. Results and discussion

3.1. Synthesis

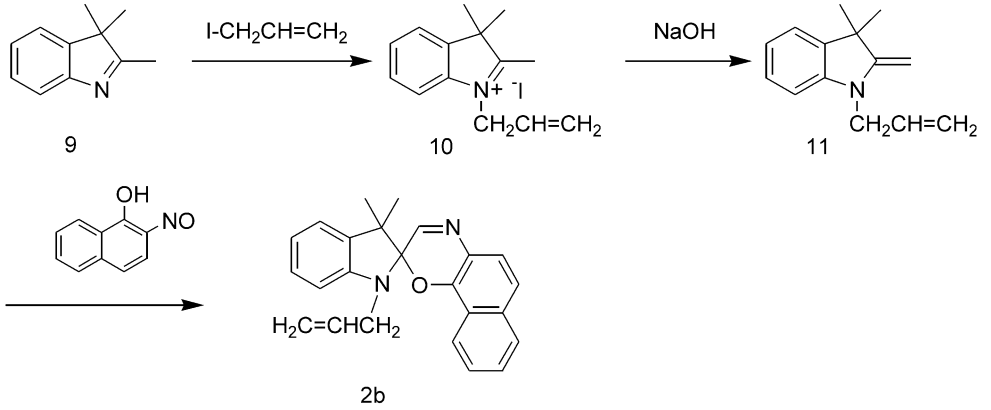
The target dyes were spironaphth[1,2-b]oxazines having an allyl substituent (**2b**) or a 3-(diethoxymethylsilyl)propyl group (**2c**). Dye **2b** was obtained in very low yield by the reaction sequence shown in Scheme 2. The indolenium iodide (**10**) produced from 2,3,3-trimethyl-3H-indole (**9**) and allyl iodide was treated with NaOH solution and the resultant allyl-substituted indoline (**11**) was separated from NaI prior to the reaction with 2-nitroso-1-naphthol. This procedure is hereinafter referred to as Method A.

Since spirooxazine **2c** has a diethoxymethylsilyl group that is readily hydrolyzed under basic conditions, aqueous NaOH could not be used in its synthesis. Therefore, in a modified procedure (Method B), the indolenium iodide formed by the reaction of the trimethylindole and diethoxy(3-iodopropyl)methylsilane was treated with anhydrous triethylamine. The resultant indoline was reacted with the nitrosonaphthol without isolation, giving a crude product mixture containing two photochromic compounds. Spirooxazine **2c** was isolated by repeated column chromatography, but the second photochromic compound could not be isolated in pure form.

In order to shed light on the nature of the second photochromic compound, Method B was employed in the synthesis of spirooxazine **2a**. In this case, two photochromic compounds were obtained. The second product, a minor impurity, could be obtained by repeated column chromatography. The ^{1}H NMR spectrum of the second product contained two pairs of signals of comparable intensities that were attributed to the methyl groups on the *N*-atom and C-3 positions of the indoline ring. The molecular ion peak observed in the mass spectrum of this product was consistent with the formation of a compound composed of one naphthoxazine ring and two indoline rings. Although the position to which the second indoline moiety was attached could not be determined by NMR, due to impurities in the sample, we were able to characterise the structure based on previous results [11]. With this in mind, the most likely structure of the second product obtained when dye **2a** was employed in Method B is that of compound **3**.

In Method B, nitrosonaphthol was added to a solution containing the indoline, producing a product having two indoline groups. While it would be expected that the formation of compound **3** is suppressed when the indoline is the limiting reactant, a dropwise addition of the indoline to nitrosonaphthol did not suppress the formation of **3**.

Taking into account the results of previous related studies [6,7,12], we believe that the title spirooxazines can be used for the preparation of photochromic siloxane polymer materials via either a hydrosilation (**2b**) or hydrolysis/polycondensation (**2c**) reaction.

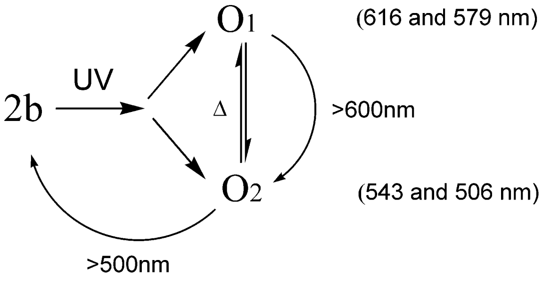


Scheme 2. Synthesis of dye **2b** via method A.

3.2. Photochromism

Spironaphth[1,2-b]oxazine **2b** was photochromic in organic solvents. The color changed from colorless to blue upon UV irradiation, but the color faded immediately at 298 K. At low temperature (183 K), the color change lasted long enough to be recorded by a spectrophotometer (cf. Fig. 1). When a hexane solution of **2b** was irradiated for 2 min with UV light, the visible absorption spectrum showed maxima at 616 and 579 nm and shoulders at 543 and 506 nm. Decoloration of this solution occurred upon irradiation with light having $\lambda > 500$ nm. On the other hand, irradiation of the colored solution for 6 min with light having $\lambda > 600$ nm did not cause decoloration. Instead, the intensities of two absorption maxima decreased and the two shoulders increased in intensity. When the light having $\lambda > 600$ nm was removed, the original spectrum was gradually restored and an isosbestic point was observed at 560 nm.

The colored open (merocyanine) form consists of four geometric isomers, *EZ*, *EE*, *ZZ* and *ZE*, which have comparable stability and are thermally in equilibrium. Two of them afford the absorption maxima denoted by O_1 (Scheme 3) and the other two isomers produced the two shoulders denoted by O_2. O_1 and O_2, are slowly isomerised to the colorless spirooxazine **2b** by visible light having $\lambda > 500$ nm. In this regard, O_1 does not change directly to **2b**, but instead it is transformed into **2b** via the intermediacy of O_2 following the absorption of light having $\lambda > 600$ nm. This double photochromism was also observed with spirooxazine **2c**.



Scheme 3. Double photochromism of **2b**.

4. Conclusions

The present spirooxazines have the properties required in a non-destructive read-out system

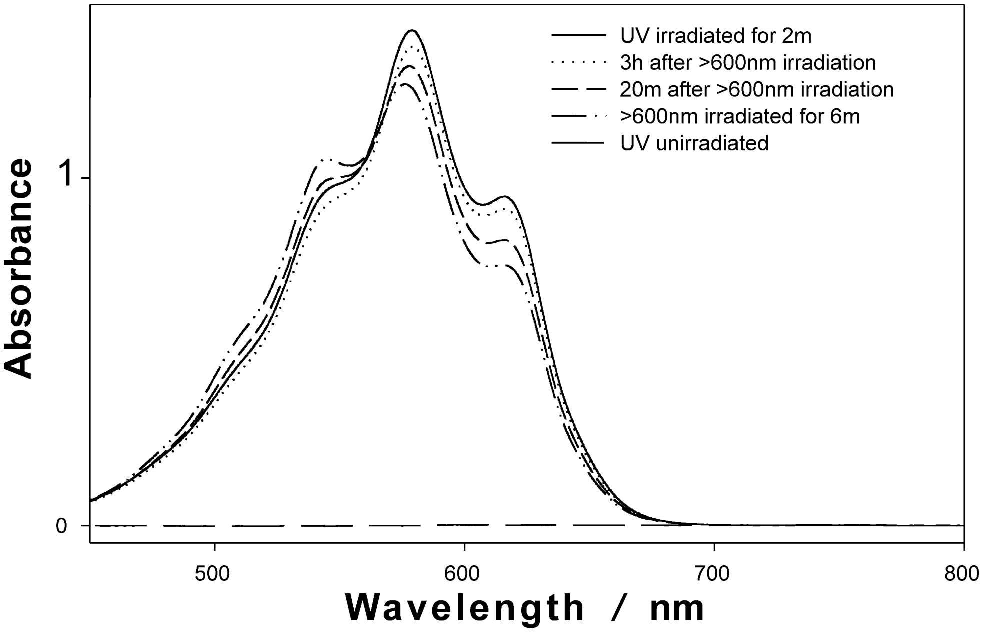


Fig. 1. Photochromism of **2b** in hexane at 183 K.

possessing light-induced information memory. For recording and erasing of information, UV light and visible light of $\lambda > 500$ nm are used, respectively. As long as the light having $\lambda > 600$ nm is used for the reading-out, destruction of memory does not occur.

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