Synthesis of photochromic chelating spironaphthoxazines

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Abstract

Some novel spiroindolinonaphthoxazines, containing chelating functional groups were synthesized in order to evaluate their photochromic properties. Their physical and spectroscopic characteristics (UV, 1H-NMR, absorption and elemental analysis) were determined. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Spirooxazines represent an important class of photochromic compounds. They belong to the class of compounds, that exhibit both normal and reverse photochromism [1]. The photochromic reaction of these compounds is the reversible het erotelytic cleavage and re-binding of the pyranyl C(spiro)–O bond, yielding a colored open and colorless closed form, respectively. Photochromic spirooxazines have been a subject of intensive investigations of their potential applications, including light filters and optical devices [2,3], photochromic liquid crystals [4–6], photochromic plastics [7], photochromic substances useful in lenses [8,9], metal complexing agents [10–13] and erasable optical disks [14].

Spirooxazines belong to a class of photochromic compounds closely related to spiropyrans in which the carbon atom in the methine bridge is replaced by a nitrogen atom. Their photo fatigue resistance is much better than that of spiropyrans [15]. It has been reported that spiropyrans, which possess a coordinating group next to the pyranyl O atom [16–21], can act as chelating agents in the colored open form.

In this work we present the synthesis of spironaphthoxazine derivatives containing suitable groups which are capable of acting as chelating agents [10].

2. Results and discussion

The most common method employed for the synthesis of spironaphthoxazine is condensation of diklydene heterocycle with o-nitrosanaphthols in polar organic solvents, such as methanol [22] or chlorinated lower aliphatic hydrocarbons.

The present photochromic spironaphthoxazines were prepared by the reaction of 1,3,3-trimethyl-2-
methylene indoline, or 1-butyl-3,3-dimethyl-2-methylene indoline, or the corresponding benz[e]indolium perchlorates compounds 1,3,3-trimethyl-benz[e]indolium perchlorates, or 1-butyl-3,3-dimethyl benz[e]indolium perchlorates with the corresponding o-nitrosonaphtols.

The synthesis of dyes $3(a,b)$ involves two stages given in Scheme 1. The 1-nitroso-2,3-dihydroxynaphthalene was prepared by a direct nitrozation of 2,3-dihydroxynaphthalene in aqueous solution. The photochromic dyes $3(a,b)$ were synthesized by a direct condensation of $1(a)$, or $1(b)$ with o-nitroso-2,3-dihydroxynaphthalene in dichlorethane.

Spironaphthoxazines $8(a–d)$ were prepared in three steps, which include the preparation of 2-hydroxy-3-(benzothiazol-2-yl)naphthalene (6) [23], followed by nitrozation (Scheme 2) and condensation (Scheme 3) with the corresponding alkylidene heterocycles $1(a–d)$. Generally the yield of crude product in the last condensation step does not exceed 40%.

The photochromic compound $3a$ with hydroxy group next to the pyranyl oxygen was alkylated with dimethylsulfate. In this way we obtained a photochromic compound with a methoxy group (Scheme 4).

Characterization data for dyes $3(a,b)$, $8(a–d)$ and $10$ are given in Table 1. All compounds are pale yellow in the solid state after crystallization from non polar solvents such as heptane. All they give colorless or pale yellow solutions (Figs. 1a and 2a) in heptane, hexane or cyclohexane in which the closed spironaphthoxazine form is dominating and blue or green solutions (Figs. 1b
Table 1

Characterization data for dyes 3(a,b), 8(a–d) and 10

<table>
<thead>
<tr>
<th>Dye</th>
<th>Yield % of purified product (reaction time, h)</th>
<th>m.p. (°C)</th>
<th>$\lambda_{\text{max}}$ (nm) merocyanine (CH$_2$Cl$_2$)</th>
<th>Molecular formula</th>
<th>Analysis % found/calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>18 (1)</td>
<td>145–148</td>
<td>600</td>
<td>C$<em>{22}$H$</em>{20}$N$_2$O$_2$</td>
<td>76.74/5.81, 8.14</td>
</tr>
<tr>
<td>3b</td>
<td>15 (2)</td>
<td>150–152</td>
<td>595</td>
<td>C$<em>{22}$H$</em>{20}$N$_2$O$_2$</td>
<td>76.74/5.93, 8.04</td>
</tr>
<tr>
<td>8a</td>
<td>18 (2)</td>
<td>214–215</td>
<td>645</td>
<td>C$<em>{29}$H$</em>{33}$N$_3$O$_3$</td>
<td>74.90/5.02, 9.30</td>
</tr>
<tr>
<td>8b</td>
<td>16 (2)</td>
<td>142–143</td>
<td>650</td>
<td>C$<em>{29}$H$</em>{29}$N$_3$O$_3$</td>
<td>74.34/5.77, 8.35</td>
</tr>
<tr>
<td>8c</td>
<td>15 (2)</td>
<td>228–230</td>
<td>655</td>
<td>C$<em>{33}$H$</em>{23}$N$_3$O$_3$</td>
<td>77.79/5.01, 8.24</td>
</tr>
<tr>
<td>8d</td>
<td>13 (2)</td>
<td>200–202</td>
<td>660</td>
<td>C$<em>{36}$H$</em>{37}$N$_3$O$_3$</td>
<td>78.12/5.61, 7.59</td>
</tr>
<tr>
<td>10</td>
<td>10 (2)</td>
<td>195–197</td>
<td>585</td>
<td>C$<em>{23}$H$</em>{22}$N$_2$O$_2$</td>
<td>76.92/5.61, 7.69</td>
</tr>
</tbody>
</table>

Scheme 3.

Scheme 4.
Fig. 1. Absorption spectra of 1,3,3-trimethyl-5'-hydroxyspiro(indolino-2,2(2H-1)napthoxazine) (3a), 1-butyl-3,3-dimethyl-5'-hydroxyspiro(indolino-2,2(2H)naphthoxazine (3b) and 1,3,3-trimethyl-5'-methoxyspiroindolino-2,2(2H-1)naphthoxazine (10) 4.5×10⁻⁵ M in hexane (a) and 2.4×10⁻⁴ M in CH₂Cl₂ (b) at 25 °C.
Fig. 2. Absorption spectra of 1,3,3-trimethyl-5′-(benzothiazol-2-yl)-spiroindolino-2,3′-naphth(2,1-b)(1,4)oxazine (8a); 1-butyl-3,3-dimethyl-5′-(benzothiazol-2-yl)-spiroindolino-2,3′-naphth(2,1-b)(1,4)oxazine (8b); 1,3,3-trimethyl-5′-(benzothiazol-2-yl)-spironaphthindolino-2,3′-naphth(2,1-b)(1,4)oxazine (8c); 1-butyl-3,3-dimethyl-5′-(benzothiazol-2-yl)-spironaphthindolino-2,3′-naphth(2,1-b)(1,4)oxazine (8d) 6.5×10⁻⁵ M in hexane (a) and 0.3×10⁻³–1.6×10⁻³ M in CH₂Cl₂ (b) at 25 °C.
and 2b) in methylene chloride in which the intensively colored merocyanine form exists. In ethanol and acetone, solutions are nearly colorless because of the equilibrium between the merocyanine and spironaphthoxazine form existing in them. Temperature has no effect on ethanol solutions, but some acetone solutions become colorless on heating.

All compounds are reversibly photochromic in appropriate solvents. An initially nearly colorless ethanol or acetone solution turns to intensive blue or green color by about 1 min of exposure to a 250 W Hg-lamp and becomes colorless again a few seconds after irradiation. Longer irradiation decomposes the compounds.

The merocyanine form of the synthesized photochromic compounds appears to give chelate complexes with transition metal ions as Cr$^{3+}$, Cu$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and Fe$^{2+}$ in solvents of different polarity. The studies are in progress.

3. Experimental

Melting points are determined on a Kofler apparatus and are uncorrected. $^1$H NMR spectra of the dyes are obtained in CDCl$_3$ on a Bruker 500 MHz spectrometer. Absorption spectra are measured on a Specord UV–VIS spectrophotometer (Carl-Zeiss, Jena) in hexane and dichloromethane solutions. Irradiation of the cell contents is performed at approximately 25 cm distance from a 250 W Hg-lamp.

3.1. Preparation of 1,3,3-trimethyl-5-$\alpha$-hydroxyspiro(indolino-2,2(2H)-naphthoxazine) (3a) and 1-butyl-3,3-dimethyl-5-$\alpha$-hydroxyspiro(indolino-2,2-(2H)naphthoxazine (3b)

3.1.1. Preparation of 1-nitroso-2,3-dihydroxynaphthalene

2,3-Dihydroxynaphthalene (0.1 mol) was dissolved in a warm solution of 0.1 mol sodium hydroxide in 50 ml of water. The solution was cooled to 0 °C in an external ice bath and 0.1 mol sodium nitrite was added with stirring. After 1 h 0.3 mol of dilute sulphuric acid was added, ensuring that the temperature was kept at 0 °C. The nitroso-2,3-dihydroxynaphthalene gradually separated during the reaction. The product was then filtered by suction, washed with water and dried in a vacuum desiccator. The nitroso compound was obtained in a reasonably pure form as indicated by TLC analysis (CHCl$_3$:CH$_3$OH). The compound was used directly in the synthesis of spirooxazines 3a and 3b.

3.1.2. Preparation of the photochromic dyes 3a and 3b

1-Nitroso-2,3-dihydroxynaphthalene (2) (0.01 mol) was refluxed in 50 ml 1,2-dichloroethane and to the hot solution was added dropwise over 15 min a solution of 0.01 mol 1,3,3-trimethyl-2-methylene indoline in 10 ml of 1,2-dichloroethane or 0.01 mol 1-butyl-3,3-dimethylindolenium perchlorate with 0.02 mol triethylamine. The mixture was then refluxed for 1 h and cooled. After standing for some time, the precipitated product was filtered by suction and washed with ethanol. The solid was then dissolved in acetone and boiled with activated charcoal gently for 5 min. The solution was filtered hot to remove the charcoal and concentrated. The product was purified by column chromatography, silica/CH$_2$Cl$_2$:petroleum ether (1:1), and further purified by recrystallization from heptane.

3.2. Preparation of the photochromic dyes 8(a–d)

3.2.1. Preparation of 2-hydroxy-3-(benzothiazol-2-yl)naphthalene (6)

2-Hydroxy-3-naphthalenecarboxylic acid (0.01 mol) and 0.011 mol 2-aminothiophenol were dissolved in 21 ml boiling toluene. After cooling to 90 °C 0.01 mol PCl$_3$ in 5.4 ml toluene was added dropwise to the solution. The mixture was then refluxed for 2 h and then cooled to 60 °C and mixed with 40 ml methanol. The precipitated product was filtered and washed with methanol. The product was dried under vacuum. Yield—82%.

3.2.2. Preparation of 1-nitroso-2-hydroxy-3-(benzothiazol-2-yl)naphthalene. (7)

2-Hydroxy-3-(benzothiazol-2-yl)naphthalene (0.01 mol) was dissolved in 36 g glacial acetic acid and by 0–5 °C treated with 0.01 mol NaNO$_2$. The mixture was stirred 3 h at 5 °C and then was added to 100 ml of ice water. The precipitated
product was then filtered off, washed with ice water and dried. Yield = 98% m.p. = 179 °C [23].

3.2.3. Preparation of 1,3,3-trimethyl 5’-(benzo-thiazol-2-yl)-spiroindolino-2,3’-napth(2,1-b)-(1,4)oxazine (8a)

(7) (0.01 mol) was refluxed in 100 ml ethanol and to the hot solution dropwise were added over 15 min a solution of 0.01 mol 1,3,3-trimethyl-2-methylene-indole (1a) in 10 ml ethanol and 0.5 ml piperidine. The mixture was refluxed for 2 h and cooled. The precipitated product was filtered off and washed with ethanol. The crude product was purified by column chromatography (Al2O3/CH2Cl2).

3.2.4. Preparation of 1-butyl-3,3-dimethyl 5’-(benzothiazol-2-yl)-spiroindolino-2,3’-napth(2,1-b)-(1,4)oxazine (8b);

1,3,3-trimethyl 5’-(benzothiazol-2-yl)-spironaphthindolino-2,3’-napth(2,1-b)-(1,4)oxazine (8c);

1-butyl-3,3-dimethyl 5’-(benzothiazol-2-yl)-spironaphthindolino-2,3’-napth(2,1-b)(1,4)oxazine (8d)

(7) (0.01 mol) and 0.01 mol of 1-butyl-3,3-dimethylnaphtholinium perchlorate (1b) or 1,3,3-trimethylnaphthindolinium perchlorate (1c) or 1-butyl-3,3-dimethylnaphthindolinium perchlorate (1d) were refluxed in 100 ml ethanol. Triethylamine (0.02 mol) was added to the solution. The mixture was refluxed for 2 h and cooled. The precipitated product was filtered by suction and washed with ethanol. The crude product was purified by column chromatography, silica/CH2Cl2; petroleum ether (1:1).

3.3. Preparation of 1,3,3-trimethyl 5’-methoxy-spiroindolino-2,2’(2H-1)napthoxazine (10)

3a (0.01 mol) was dissolved in 0.01 mol NaOH in 30 ml water. Fifteen millilitres of acetone was added to the solution and then 0.02 mol dimethylsulphate were added dropwise. The mixture was stirred 1 h at room temperature. The crude product was isolated by decanting and then was dissolved in alkaline water solution and was extracted with CH2Cl2. The separated phase was distilled under reduced pressure. The crude product was purified by column chromatography, Al2O3/CH2Cl2; petroleum ether (5:95).

Characterization data, yield, m.p., absorption and elemental analysis are shown in Table 1.

3.4. NMR spectra of dyes 3a, 8(a–d) and 10

3.4.1.

Dye 3a: 6.63–7.82 (m, 10H, Ar); 1.41 (s, 6H, 2/C2CH3); 2.83 (s, 3H, N+–CH3); 7.27 (s, 1H, –N=CH), 6.64 (s, 1H, –OH).

3.4.2.

Dye 8a: 6.66–9.04 (m, 14H, Ar); 1.44 (s, 6H, 2/C2CH3); 2.80 (s, 3H, N+–CH3); 7.29 (s, –N=CH).

3.4.3.

Dye 8b: 6.71–9.05 (m, 14H, Ar); 1.42 (s, 6H, 2/C2CH3); 3.21 (s, 8H, 2/C2CH2–CH); 7.35 (s, –N=CH).

3.4.4.

Dye 8c: 7.08–9.05 (m, 16H, Ar); 1.82 (s, 6H, 2/C2CH3); 3.31 (s, 8H, 2/C2CH2–CH2); 7.50 (s, –N=CH).

3.4.5.

Dye 8d: 7.11–9.06 (m, 16H, Ar); 1.80 (s, 6H, 2/C2CH3); 3.31 (s, 8H, 2/C2CH2–CH2); 7.92 (s, –N=CH).

3.4.6.

Dye 10: 6.59–8.50 (m, 10H, Ar); 1.37 (s, 6H, 2/C2CH3); 2.84 (s, 3H, N+–CH3); 7.29 (s, –N=CH), 3.89 (s, 3H, –OCH3).

References