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Resolution and Circular Dichroism of a Non-activated Spiropyran Dye: 6-(*p*-Chlorophenylazo)-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline]

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ABSTRACT

*The non-activated spiropyran dye 6-(*p*-chlorophenylazo)-1′,3′,3′-trimethylspiro[2H-1-benzopyran-2,2′-indoline] (**2**) was synthesized and resolved by chiral stationary phase HPLC. The chiroptical properties of the optically active dye were determined by circular dichroism spectropolarimetry. © 1998 Elsevier Science Ltd. All rights reserved*

1. INTRODUCTION

Photochromic spiropyran dyes have been extensively studied due to their potential applications in many new technologies, including high-density optical data storage, optical switching, displays and non-linear optics [1, 2]. Thus far, most studies have focused on derivatives of 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (**1**) due to its propensity to undergo photochemical ring opening to a stable merocyanine form. Other *non-activated* spiropyrans lack a strong electron-withdrawing group that stabilizes the colored merocyanine form. Upon irradiation, these species give rise to photostationary states with negligible merocyanine concentrations [3–5]. The merocyanine form being prochiral, irradiation of a non-activated spiropyran should result in its efficient photoracemization; if circularly polarized light is used, the photoresolution of a non-activated spiropyran dye

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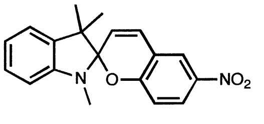
*Corresponding author. Fax: 001 613 545 6669; e-mail: lemieux@chem.queensu.ca should be possible by virtue of circular dichroism (CD) [6]. In order to estimate the theoretical limit for photoresolution of non-activated spiropyran derivatives, it is necessary to determine their chiroptical properties using CD spectropolarimetry. As part of our continuing studies on structure-activity relationships in spiropyran-merocyanine interconversions [5, 7–11], we report the resolution of the non-activated spiropyran 6-(*p*-chlorophenylazo)-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (**2**) by chiral stationary phase HPLC, and the recording of CD spectra for each enantiomer. To the best of our knowledge, only one other example of optical resolution of a spiropyran dye has been reported [12].



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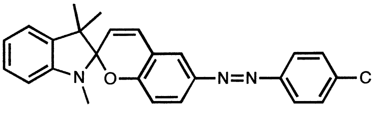

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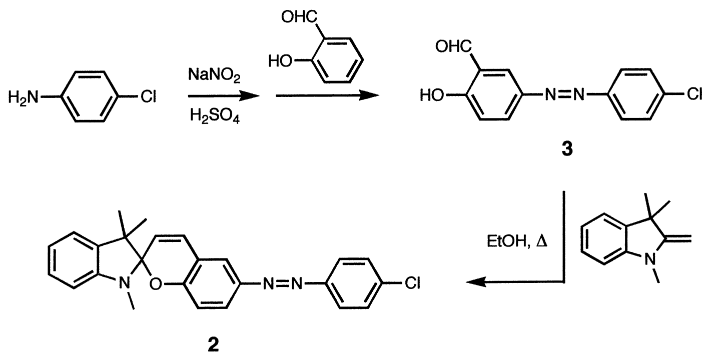
2 RESULTS AND DISCUSSION

2.1 Synthesis and optical resolution

The spiropyran **2** was prepared by reaction of 5-(*p*-chlorophenylazo)-salicylaldehyde (**3**) and Fischer base, as shown in Scheme 1. Compound **3** was obtained by coupling the diazonium salt of *p*-chloroaniline with salicylaldehyde. Resolution of **2** was achieved by semi-prep chiral stationary phase HPLC using a 25 cm × 10 mm i.d. Regis (S,S)-Whelk-O 1 column (99:1 hexanes/isopropyl alcohol, 4.5 ml/min). We were unable to achieve complete baseline resolution at the semi-prep scale, i.e. 3–5 mg per injection. Two fractions



Scheme 1.

were isolated: one enriched with the first eluting enantiomer (fraction **A**, 65% ee), the other enriched with the second eluting enantiomer (fraction **B**, 30% ee). The solutions of resolved materials were carefully shielded from light, and CD spectra were acquired in cyclohexane at room temperature. Subsequent analysis of the samples by chiral stationary phase HPLC showed no loss of optical activity. The UV spectrum of racemic **2** and CD spectra of fractions **A** and **B** are shown in Figs 1 and 2.

2.2 Chiroptical properties

As expected, the CD spectra of fractions **A** and **B** are mirror images. The spectra show split Cotton effects centered at ca. 270 nm (positive chirality for **A**, negative chirality for **B**), which arise from chiral exciton coupling between the two chromophores of the spiropyran moiety [13]. The theoretical limit for photoresolution of a chiral chromophore at a given wavelength is given by the Kuhn anisotropy factor ($g = \Delta\varepsilon/2\varepsilon$) [6]. These values were calculated from the UV and CD spectra of fraction **A** after normalization to 100% ee, and are plotted as a function of wavelength in Fig. 3. The Kuhn anisotropy factor data suggest that photoresolution of racemic **2** to a maximum enantiomeric excess of 0.075% ee could be achieved by irradiation with circularly polarized light at 253 nm. Further work aimed at investigating the chiroptical properties and potential for photoresolution of other spiropyran derivatives is in progress.

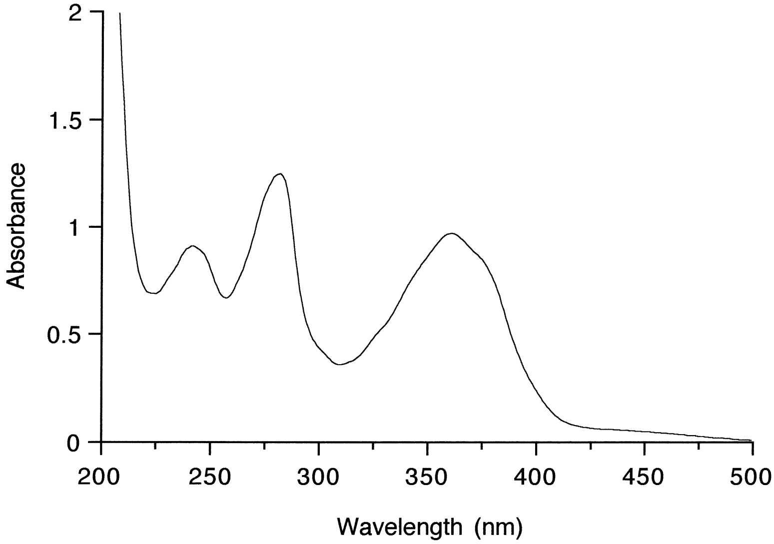


Fig. 1. UV-visible absorption spectrum of a 7×10^{-5} M solution of **2** in cyclohexane.

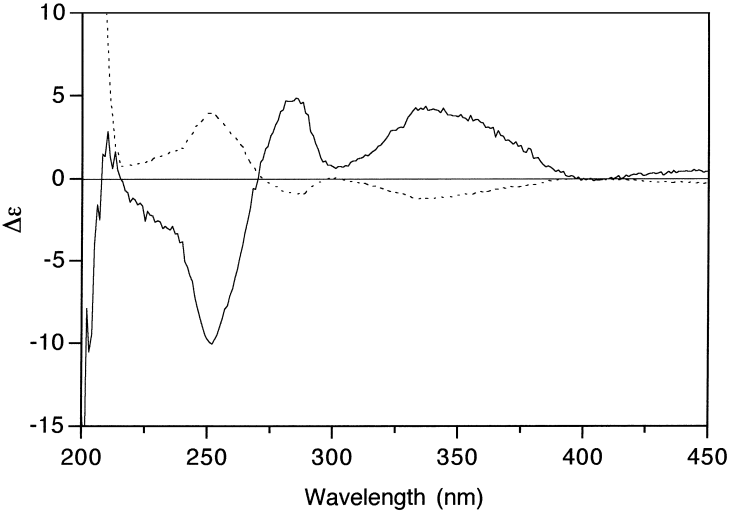


Fig. 2. Circular dichroism spectra of 5×10^{-5} M solutions of resolved **2**: fraction **A**, 65% ee (solid line), fraction **B**, 30% ee (dashed line).

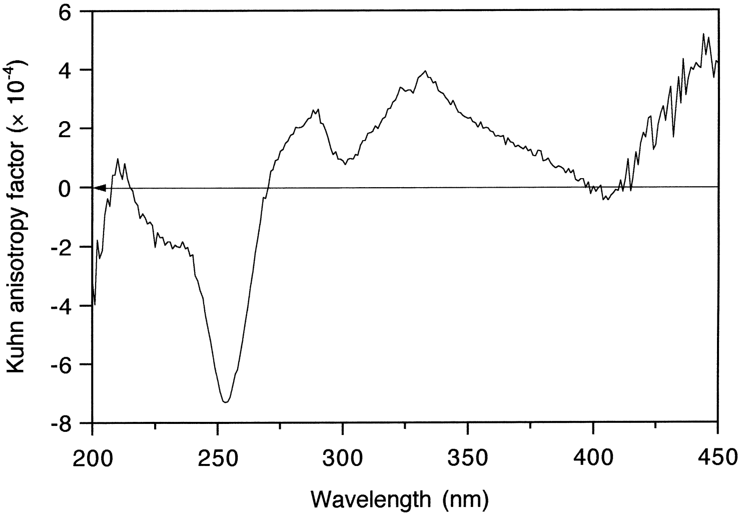


Fig. 3. Plot of Kuhn anisotropy factor values (*g*) as a function of wavelength for resolved **2** after normalization to an optical purity of 100% ee.

3 EXPERIMENTAL

3.1 General

Proton NMR spectra were recorded on a Bruker CXP-400 spectrometer in CDCl3, with tetramethylsilane as internal standard. Infrared spectra were recorded on Analet Instrument FT-IR (MAP 60) and Shimadzu FT-IR 8501 instruments using KBr pellets. UV-visible absorption spectra were recorded on a Varian Cary 3 spectrophotometer in cyclohexane. Electrospray mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer. Circular dichroism spectra were recorded on a JASCO spectropolarimeter in cyclohexane. Melting points were determined using a Fisher–Jones apparatus and are uncorrected.

3.2 Synthesis

*5-(p-chlorophenylazo)salicylaldehyde (**3**)*

To a solution of *p*-chloroaniline (2.5 g, 20 mmol) in 10% aq HCl (15 ml) cooled to 0°C was added a solution of $NaNO_2$ (1.73 g, 20 mmol) in H_2O (10 ml). The resulting cold solution was added slowly to salicylaldehyde (2.6 g, 21 mmol) in 20% aq NaOH (25 ml) kept at 0°C. After standing for 2 h, the mixture was filtered and the residue recrystallized from acetone to give 4.47 g (86% yield) of **3** as a yellow solid: mp 173°C.

*6-(p-chlorophenylazo)-1′,3′,3′-trimethylspiro[2*H*-1-benzopyran-2,2′-indoline] (**2**).*

A solution of 1,3,3-trimethyl-2-methyleneindoline (Fluka, 2.61 g, 15.1 mmol) in EtOH (10 ml) was slowly poured into a solution of **3** (4.7 g, 18 mmol) in EtOH (20 ml) and refluxed for 7 h. After cooling, the precipitate was isolated by filtration and recrystalllized from acetone/ether to give 4.46 g (71% yield) of **2** as a yellow solid: mp 179°C; 1H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 3H), 1.32 (s, 3H), 2.75 (s, 3H), 5.91 (d, 1H), 6.54 (dd, 1H), 6.81 (d, 1H), 6.82 (m, 1H), 6.95 (d, 1H), 7.11 (m, 1H), 7.21 (dd, 1H), 7.44 (d, 2H), 7.67 (d, 1H), 7.72 (dd, 1H), 7.80 (d, 2H); MS (ES) m/e 416 (M+, 21), 214 (6), 206 (10), 176 (6), 174 (100), 158 (15), 156 (16), 132 (6), 120 (6); IR (cm^{-1}) 3470 (s), 2962 (w), 1608 (m), 1483 (s), 1267 (m), 1105 (s), 960 (s), 825 (m); UV (C_6H_{12}) γ_{max} 241 (log ε 4.11), 282 (4.25), 361 (4.14); CD (fraction A, C_6H_{12}) γ_{ext} 252 ($\Delta\varepsilon -10.0$), 285 (+4.8), 337 (+4.3), 444 (+0.51).

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