Journal of Molecular Structure 1123 (2016) 426–432

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Reversible negative photochromic sulfo-substituted spiropyrans

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ARTICLE INFO

Article history:
Received 24 February 2016
Received in revised form
6 June 2016
Accepted 13 July 2016
Available online 15 July 2016

Keywords:
Negative photochromism
Spiropyran
Fatigue resistance
Proton transfer

ABSTRACT

A series of sulfonyl-containing spiropyrans exhibiting negative photochromism were designed and synthesized. The prepared compounds show more stability for the brightly colored state in the dark-adapted than the colorless state under visible irradiation. Negative photochromic properties and fatigue resistance of these compounds in solution were confirmed by UV spectroscopy with time variation. Single-crystal X-ray diffraction analysis, NMR and variable-time absorption spectra studies suggest that the negative photochromism of the compounds involved a ring-opening spiro C–O bond cleavage of the spiropyran followed by an intramolecular proton transfer.

1. Introduction

The photochromism of spiropyran derivatives has captured considerable attention due to its application potentials in the areas of optical data storage [1], optical switches [2], sensors [3], and liquid crystalline components [4], etc. The photochromic process involves a ring opening/closure electrocyclic isomerization exhibiting a photochromism under the condition of incident radiation or dark [5]. Most the reported spiropyrans show positive photochromism with a structural changing from the colorless (or light colored) ring-closed spiropyran(SP) form to the deep colored open-ring merocyanine(MC) form under ultraviolet/visible light irradiation [6]. While the negative process gives deep color in dark or a red-shifted absorption than that in the above-mentioned positive one [5,7]. The MC form prefers to present in the electronic configuration of a resonance hybrid with zwitterionic and quinoidal structures depending on the nature of substituents and solvents. One of the potential problems of those spiropyrans is that the photochromic process could exacerbate the photodegradation or poor fatigue resistance [8]. The photoresponse of these compounds is also susceptible to environmental effects [9].

Besides finding positive photochromic compounds with new structure, developing negative photochromic spiropyrans is also desirable for both highly efficient photochromism and excellent fatigue resistance. However, only few examples of the latter have been published so far [10]. Although substituent effect has been used in some spiropyran molecules to improve the thermodynamic stability of the MC form structure facilitating the negative photochromic behavior [10c,10d,11]. They were mainly nitro-compounds with the substituent position restricted on the benzopyran moiety or the N atom of indoline moiety at present [10d,11,12]. From the structural point of view, sulfo-spiropyrans with substituent position on the phenyl of indoline moiety could improve the electrocyclic cleavage of the C_{spiro}–O bond not only by electron-withdrawing effect but also by the proton-transfer from the sulfo group to the pyran oxygen [10a,11,13]. Moreover, the self-calibration of proton transfer between –OH and $-SO_3H$ can also prevent the pH change in the system, just like a buffer [14].

In fact, a recent literature has made use of $-SO_3H$ as a strong acid group for a photoresponsive potassium salt of ring-closed SP-sulfonic acid [15]. But the fatigue resistance and substituent effects on the material have not been investigated. And its synthesis via the methylation with methyl iodide from 4-hydrazinobenzenesulfonic acid is also relatively tedious and expensive fall on lower yield. Herein we report a series of indoline-SO_3H substituted spiropyrans with different substituents on the benzopyran moiety. Their structures were characterized by elemental analysis, IR and NMR spectra, as well as the single-crystal X-ray diffraction analysis. Their negative photochromic properties and fatigue resistance were studied by UV spectroscopy with visible light irradiation and in dark.

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http://dx.doi.org/10.1016/j.molstruc.2016.07.050
0022-2860/

2. Experimental

2.1. Materials and measurements

Unless otherwise noted, the reagents and solvents were used as received from commercial suppliers without further purification. Elemental analysis was carried out with a Vario EL III elemental analyzer. Infrared spectrum was recorded in the range of (4000–400) cm^{-1} on a Nicolet Magna 750 FT-IR spectrometer. The ^1H NMR spectrum of the compound was tested on a Mercury Plus-500 spectrometer by using TMS as the internal standard and DMSO-d_6 as the solvent. Mass spectra were recorded on a thermo Finnigan LCQ Advantage LC/Mass detector instrument. The X-ray single-crystal diffraction was measured on Rigaku Mercury 70 CCD diffractometer. Photoluminescent spectrum was recorded with an F-7000 fluorescence spectrophotometer with the excitation and emission slit widths at 2.5 nm.

2.2. Synthesis of the compounds

As illustrated in Scheme 1, The investigated negative photochromic spiropyran derivatives **2a**, **2b**, **2c** were easily obtained by the sulfonation of indoline and the subsequent Prins reaction of sulfonate-substituted indolenium with the corresponding salicylaldehyde compounds salicylaldehyde, 5-methylsalicylaldehyde and *5*-nitrosalicylaldehyde, respectively [16].

2.2.1. Synthesis of the ***2a***

To a solution of 1,3,3-trimethyl-2-methyleneindoline (2.00 mL, 11.3 mmol) was added oleum (50%, 6 mL) and stirred at ambient temperature for 4 h followed by heating to 80 °C for 10 h. After cooling to ambient temperature, the acid was poured into ice water and neutralized with KOH to basic, then $Ba(OH)_2$, K_2CO_3 was added orderly and filtered, the filtrate was concentrated in vacuo and the residue was purified by recrystallization from ethanol to afford light-yellow solid (**1**). ^1H NMR (DMSO-d_6, 400 MHz) δ: 1.27 (s, 6H), 3.00 (s, 3H), 3.88 (s, 2H), 6.56–6.58 (d, 1H), 7.34–7.38 (t, 2H).

A solution of potassium 1,3,3-trimethyl-2-methyleneindoline-6-sulfonate (**1**) (0.1455 g, 0.5 mmol) and salicylaldehyde (50 μL, 0.5 mmol) in 15 mL ethanol and water (3:2, v/v) was refluxed for 12 h. After cooling to ambient temperature, the pH value of the resultant solution was adjusted to approximately 3 by slow addition of 2 mol/L HCl, and then the orange-yellow crystals were grown by slow evaporation at room temperature for 4 days. The single crystals of **2a** were collected by vacuum filtration, washed with ethyl acetate, and dried. ^1H NMR (DMSO-d_6, 400 MHz) δ: 1.09 (s, 3H), 1.21 (s, 3H), 2.65 (s, 3H), 5.76–5.79 (d, 1H), 6.46–7.40 (8H).

2.2.2. Synthesis of the ***2b***

A mixture of (**1**) (0.1455 g, 0.5 mmol) and 5-methylsalicylaldehyde (0.0681 g, 0.5 mmol) in 15 mL ethanol was refluxed for 12 h. After cooling to ambient temperature, the pH value of the resultant solution was adjusted to approximately 3 by slow addition of 2 mol/L HCl, then the orange-red solid of **2b** was collected and dried. ^1H NMR (DMSO-d_6, 400 MHz) δ: 1.09 (s, 3H), 1.21 (s, 3H), 2.19 (s, 3H), 2.63 (s, 3H), 5.73–5.76 (d, 1H), 6.44–7.38 (7H).

2.2.3. Synthesis of the ***2c***

A mixture of (**1**) (0.1455 g, 0.5 mmol) and 5-nitrosalicylaldehyde (0.0836 g, 0.5 mmol) in 20 mL ethanol was refluxed for 12 h. After cooling to ambient temperature, the pH value of the resultant solution was adjusted to approximately 3 by slow addition of 2 mol/L HCl, then the orange-yellow solid of **2c** was collected and dried in vacuum. ^1H NMR (DMSO-d_6, 400 MHz) δ: 1.13 (s, 3H), 1.22 (s, 3H), 2.68 (s, 3H), 6.00–6.03 (d, 1H), 6.53–8.23 (7H).

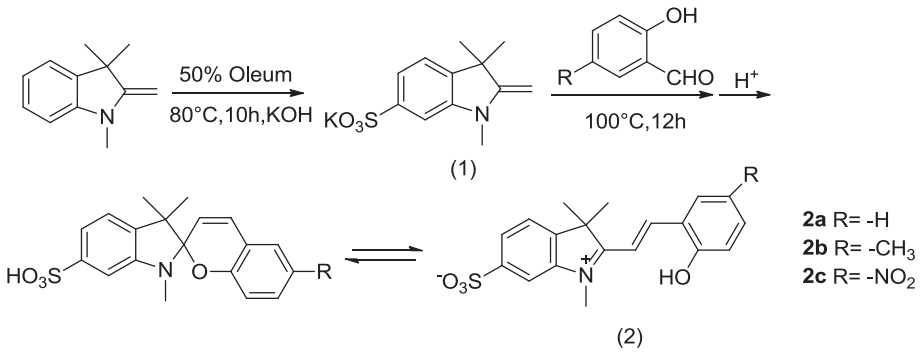
2.3. X-ray data collection and structure determination

Single crystal X-ray intensity data of the spiropyran **2a** was collected on a Rigaku Mercury 70 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293(2) K by using an ω-2θ scan mode. Intensity data were corrected for Lorentz and polarization effects as well as for an empirical absorption. The structures were solved by the direct methods. Systematic absences indicated either space group *P-1* or *P2(1)/c*, and the structure was solved in *P-1*. The presence of a centre of inversion and 2_1 screw axis were identified and the structure converted to centre *P2(1)/c* which was demonstrated to be correct by successful refinement [17]. Coordinates of the heavy atoms were obtained from an *E*-map. Other non-hydrogen atoms were generated from successive difference Fourier syntheses. The positions of the water molecules were generated from difference Fourier maps with restrained (DFIX) treatment, the positions of other H atoms were added theoretically and riding on their parent carbon atoms before the final cycle of refinement. The final refinement was performed by full-matrix least-squares method on F^2, with anisotropic displacement parameters for all non-hydrogen atoms. All calculations were performed using the SHELXTL program. The crystallographic data and experiment details for structural analysis are summarized in Table 1.

3. Results and discussion

3.1. Crystal structure

The single-crystal structural analysis revealed that the



Scheme 1. Synthetic route for the spiropyrans.