



Substituent effect on the acid-induced isomerization of spiropyran compounds

Lixia Cui^a, Honghong Zhang^a, Guomei Zhang^a, Ying Zhou^a, Li Fan^b, Lihong Shi^a, Caihong Zhang^{a,*}, Shaomin Shuang^a, Chuan Dong^{b,*}

^a School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China

^b Institute of Environmental Science, Shanxi University, Taiyuan 030006, China

ARTICLE INFO

Article history:

Received 19 July 2017

Received in revised form 23 April 2018

Accepted 29 April 2018

Available online xxxx

Keywords:

Spiropyran

Absorption spectrum

Fluorescence spectrum

pK_a

Hammett constant

ABSTRACT

Spiropyran compounds are well known as an isomeric system, the closed spiropyran (SP) could be converted into the open merocyanine (MC) via acid-induced because stable protonated merocyanine (MCH) were formed by combination of MC and H^+ . In order to understand how the substituent affect the isomerization of spiropyran. A series of the chromene 7-substituted spiropyran compounds were designed and synthesized. The photophysical properties of them were studied comparatively by UV-absorption and fluorescence spectra in different pH. The results demonstrated that the various substituents influenced not only the photophysical properties of SP, MC and MCH forms, but also the pK_a of the MC-MCH transformation. There was a good linearity relationship between the pK_a and the Hammett constant of substituent, the pK_a was smaller when the Hammett constant of substituent was larger.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

There has been a continuing interest in the isomerization of spiropyran in recent years. Spiropyran compounds are a class of important photochromic compounds, which have a colorless ring-closed “spiropyran” (SP) form that can be converted into the colored open “merocyanine” (MC) form by UV irradiation [1–5]. Furthermore, it also takes place ring opening in the presence of an acid to form protonated merocyanine (MCH) and then converts back to the closed spiropyran form (SP) with the addition of a base [6–10]. In many applications, such as biological probes [11–13], liquid crystals [14], nanoporous conducting particles [15–17], molecular switches [18–22] were designed based on the acid-induced SP-MC isomerization. An advantage of isomerization of spiropyran compounds is the dramatic difference in the photophysical properties of the two isomers, only MC form can emit fluorescence. Acid-induced is beneficial to stabilization of polar MC form and can affect its photophysical properties [23–28]. Exploiting the changes in the photophysical properties of the compounds accompanying their structures will be helpful for the development of the compounds applicable in the fluorescence probes, molecular switches and functional materials.

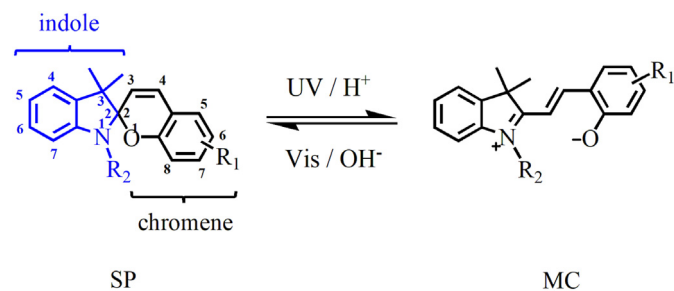
When suitable substituents were introduced the chromene ring and indole ring of SP (Scheme 1), the transformation from “SP” to “MC” by

acidification should be affected and the tunable pK_a values in certain pH range could be achieved. Raymo's group designed a switch based on the chromene 6-nitro substituted spiropyran, the results showed that the electron-withdrawing group enhanced the interconversion between SP and MC states [29]. Chan's group incorporated an oxime moiety [30] and a pH-responsive moiety [31] onto the chromene 8- of the spiropyran, and designed ratiometric pH fluorescence probes based on the excited state intramolecular proton transfer mechanism. Meizhen Yin's group designed the new extreme pH sensors by the introduction of the bulky substituent benzoic acid at the indole N-position and the electron-withdrawing carboxyl group at the indole 6-position of spiropyran [32]. It was clear that the chromene 6-, 8- and indole N-substituted spiropyran compounds significantly affect the molecular charge distribution and the process of intramolecular charge transfer of MC state. To the best of our knowledge, less attention has been paid to the chromene 7-position of spiropyran, even less was known how the various substituents with different electron withdrawing or donating power to affects the SP-MC isomerization and the pH range of their control.

In the paper, we designed and synthesized a series of the chromene 7-substituted spiropyran compounds, the photophysical properties of them were studied comparatively by UV-absorption and fluorescence spectra under pH stimulation. The results showed that pK_a values of the compounds changed gradually accompanying their different substituents ($-Cl$, $-Br$, $-H$, $-CH_3$, $-OCH_3$ and $-N(CH_2CH_3)_2$). As we expected, the chromene 7-substituted spiropyran had a slight adjustment on the pK_a of the MC-MCH transformation. This study opened a new

* Corresponding authors.

E-mail addresses: chzhang@sxu.edu.cn (C. Zhang), dc@sxu.edu.cn (C. Dong).



Scheme 1. The molecular structure of spiropyran.

way to design spiropyran-based fluorescence probes, molecular switches and biological materials.

2. Experiment

2.1. Materials

All chemicals and solvents were analytical grade and were used without further purification. 2,3,3-tetramethyl-3H-indole, ethyl iodide, 4-(dimethylamino)benzaldehyde, 2-hydroxy-4-chlorobenzaldehyde, 2-hydroxy-4-bromobenzaldehyde, 2-hydroxy-4-methoxybenzaldehyde, 2-hydroxy-4-methylbenzaldehyde and 2-hydroxybenzaldehyde were purchased from the Sigma-Aldrich company. All other chemicals were commercially available from the Beijing chemical reagent company.

2.2. Instruments

All reactions were monitored by thin-layer chromatography on glass plates coated with silica gel GF₂₅₄ (0.25 mm). ¹H NMR and ¹³C NMR spectra were collected on a 400 MHz spectrometer. High-resolution mass spectra were obtained on a Bruker Autoflex mass spectrometer (MALDI-TOF).

UV-absorption spectra were recorded on a Shimadzu UV-265 spectrophotometer (Tokyo, Japan). Fluorescence excitation and emission spectra were measured on a Hitachi F4500 spectrofluorometer (Tokyo, Japan). A PO-120 quartz cuvette (10 mm) was purchased from Shanghai Huamei Experiment Instrument Plants, China. Fluorescence measurements were carried out with excitation and emission slit width of 5 nm.

2.3. Preparation and Characterization of Compound A–F

The synthesis routes of A–F were summarized in Scheme 2. Compound 2 (1-Ethyl-2,3,3-trimethyl-3H-indolinium iodide) was synthesized following the literature methods [33]. A mixture of 3.20 g (20.00 mmol) 2,3,3-trimethyl-3H-indinium and 3.58 g (23.00 mmol)

ethyl iodide was refluxed in 60 mL of acetonitrile for 24 h. Upon cooling to room temperature, the crude solid precipitated. It was filtered off and washed with ether to give 5.60 g of pink crystals (89%).

1,2,3,3-tetramethyl-3H-indolinium iodide (1.88 g, 10 mmol), 4-substituted 2-hydroxy-benzaldehyde (10 mmol) and 2.0 mL piperidine were dissolved in 25 mL of CH₃CH₂OH, and the reaction mixture was refluxed with stirring for 12 h and then the solvents were evaporated in reduced pressure. The residue was purified by column chromatography on silica gel to give target compounds. Yield: 45–59%. The structure of A–F fully characterized by ¹H NMR, ¹³C NMR and HRMS-ESI. (see the Fig. S4–Fig. S21).

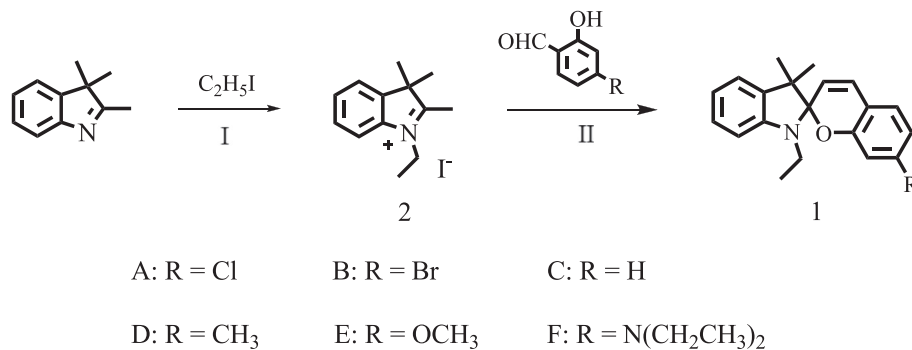
2.4. General UV–Vis and Fluorescence Spectra Measurements

The stock solutions of the A–F (0.2 mM) were prepared in DMF. And phosphate buffer saline (PBS) buffer was prepared in deionized water. The solutions for spectroscopic determination were prepared by diluting the stock solution with 50 mM buffer (containing 100 mM NaCl for constant ionic strength) at various pH values in a 1 cm quartz cell (totally 3 mL). UV–vis and fluorescence spectra were obtained in DMF: PBS (1: 9 v/v, PBS buffer, pH 7.4) solutions. After addition of analytes for 10 min, spectra could be measured. All spectroscopic experiments were carried out at room temperature. The desired solution pH was obtained by addition a certain amount of NaOH (0.1 M) or HCl (0.1 M) to adjust.

3. Results and Discussion

3.1. UV–Vis Absorbance Spectra of Compounds (A–F) in Different pH

In order to know how the different substituents to affect the SP–MC isomerization, six chromene 7-substituted spiropyran compounds (A–F) with different electron withdrawing or donating power (–Cl, –Br, –H, –CH₃, –OCH₃ and –N(CH₂CH₃)₂) were synthesized. We first investigated their UV–vis absorbance spectroscopic properties in a mixture of DMF: buffer (1: 9, 50 mM PBS buffer) at the concentration of 50 μM and the detailed experimental data were summarized in Table 1. Fig. 1 showed the UV–vis absorption spectra of compound A under the different pH. From Fig. 1, it was found that compound A exhibited two absorbance bands about 300 and 530 nm at pH = 8.0. With decreasing pH of the solution, the intensity of absorption bands at 300 and 530 nm decreased and a new band was increased at 422 nm, two clear isosbestic points at 320 and 480 nm were observed. When the pH was about 2.0, the absorption bands at 530 and 300 nm disappeared and only a sharp absorption band at 422 nm was observed. The phenomenon was reversible when the pH value was changed from 8.0 to 2.0 and back to 8.0. Meanwhile, the color of the solution changed from purple to shallower, then to yellow accompanying the pH change



I) CH₃CN, reflux, 24h II) Piperidine, EtOH, reflux, 10h

Scheme 2. The synthesis route of compound A–F.

Download English Version:

<https://daneshyari.com/en/article/7668062>

Download Persian Version:

<https://daneshyari.com/article/7668062>

[Daneshyari.com](https://daneshyari.com)