

Synthesis, crystal structure and photochromism of a novel spiro[indoline–naphthalene]oxazine derivative



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HIGHLIGHTS

- A new spirooxazine derivative was designed and synthesized.
- X-ray diffraction of the title compound has been reported.
- Photochromic properties were studied by means of UV/visible.
- The fluorescence emission spectra in solvents was analyzed.

ARTICLE INFO

Article history:

Received 5 December 2014

Received in revised form 27 January 2015

Accepted 29 January 2015

Available online 7 February 2015

Keywords:

Crystal structure

Spiroindolinonaphthooxazine

Photochromism

Acidichromism

Fluorescence properties

ABSTRACT

A new spiro[indoline–naphthalene]oxazine derivative, 12-methoxy-14,14-dimethyl-17-(piperidin-1-yl)-7,8,14,15a-tetrahydro-4bH-naphtho[1'',2'':5',6']-[1,4]oxazino[3',2':2,3][1,4]oxazino[4,3-a]indole (**1**), was successfully synthesized, and its structure was characterized by ¹H NMR, ¹³C NMR, IR, HRMS and single-crystal X-ray diffraction method. X-ray diffraction indicates that benzene and naphthalene rings of compound **1** are almost perpendicular, and the piperidine ring at the 6'-C site is in a chair conformation. In the packing diagram, a couple of short intermolecular distances such as the intermolecular short contact are observed. The photochromic properties of compound **1** have been fully investigated in different solvents, it was found that it exhibited excellent photochromism properties in solvents.

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Introduction

Organic photochromic materials have been widely investigated because of their potential applications in molecular photonic devices such as optical memories and switching devices [1–8]. Among all kinds of photochromic compounds, because of the ability to give intense photoloration, fast thermal relaxation and excellent fatigue resistance, spiroindolinonaphthooxazine (SO) derivatives are most promising candidates for applications as multifunctional optoelectronic materials [9,10]. As illustrated in Scheme 1, the photochromism of SO derivatives is due to the photochemical cleavage of the spiro C–O bond upon UV light irradiation, which leads to the extension of π -conjugation in the colored photomerocyanine (PMC) and thus shifts the absorption to the visible region [11,12]. The colored PMC can revert to the

colorless SO form by a thermally induced ring-closure reaction when the UV light irradiation ceases.

For commercial application of multifunctional optoelectronic materials, it is essential to maintain photochromic molecules with fast photoresponse, large steady-state optical density and high fatigue-resistance [13]. In the present investigation, we report the synthesis, crystal structure and photochromism of a new SO derivative **1**. The synthetic route and the structure of compound **1** in this work were shown in Scheme 2. Interestingly, to the best of our knowledge, such a SO derivative has not been reported so far. A remarkable characteristic of compound **1** is that its indoline and naphthoxazine moieties are linked by a bridged chain. X-ray diffraction indicates that compound **1** belongs to orthorhombic system. The dihedral angles between benzene (atoms C1–C6) and naphthalene rings (atoms C14–C23) are 89.56 Å. There are four molecules in one unit cell, and the structure consists of the packing molecules with normal van der Waals. Especially, in solvents, the title compound **1** displayed excellent photochromism, acidichromism and strong fluorescence properties, indicative of an extensive

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application in future development of high-performance photochromic materials.

Experimental

General remarks

All chemicals were purchased from commercial sources, and solvents used were dried and purified by distillation before use. Melting points were determined with an X4 Micro-melting point apparatus uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker 400 MHz spectrometer with TMS as internal standard. IR spectra were recorded on a TENSOR 37 spectrophotometer using KBr disks and wavenumbers were given in cm^{-1} . Mass spectra were measured on a 7070E-HE spectrometer. Fluorescence spectra were measured on a F-2500 FL Spectrophotometer. X-ray Crystal Diffraction were measured on a Rigaku 007 Saturn 70 diffractometer.

Synthesis of 5-methoxy-2,3,3-trimethyl-3H-indole

A synthetic procedure was based on the literature method [14] with slight modifications. 4-methoxy-phenylhydrazine hydrochloride (0.223 g, 1.62 mmol) and isopropyl methyl ketone (0.139 g, 1.62 mmol) were added to glacial acetic acid (10 mL). The mixture was refluxed for 10 h with stirring. Then the mixture was cooled and neutralized with 1 M Na_2CO_3 then diluted with water (100 mL) and extracted with CHCl_3 (3×100 mL). Following the drying of the organic layer over MgSO_4 , the solvent was removed by means of evaporation. A red, viscous oil of 5-methoxy-2,3,3-trimethyl-3H-indole was obtained in high yield (95%).

Synthesis of 1-(2-Hydroxyethyl)-5-methoxy-2,3,3-trimethyl-3H-indolium Bromide

A synthetic procedure was based on the literature method [15] with some modifications. A solution of 5-methoxy-2,3,3-trimethyl-3H-indole (0.502 g, 1.60 mmol) and 2-bromoethanol (0.198 g, 2.00 mmol) in MeCN (20 mL) was maintained under N_2 and heated under reflux for 1 day. After the mixture was cooled to ambient temperature, the solvent was distilled off under reduced pressure. The resulting solid was recrystallized from CHCl_3 (35 mL), then filtered and dried, to afford the targeted compound in high yield (68%).

Synthesis of 1-nitroso-2-naphthol copper salt

1.34 g (10.00 mmol) CuCl_2 in 40 mL aqueous solution was added to the 80 mL mixed solution of tetrahydrofuran and water (1:1 v/v) containing 3.98 g (24.00 mmol) 1-nitroso-2-naphthol while stirring. The reaction was completed after 20 min at room temperature, the raw product of 1-nitroso-2-naphthol copper salt was filtered, then washed with water, and dried under an infrared heat lamp. Yield: 96%.

Synthesis of 12-methoxy-14,14-dimethyl-17-(piperidin-1-yl)-7,8,14,15a-tetrahydro-4bH-naphtho[1'',2'':5',6']1,4]oxazino[3',2':2,3][1,4]oxazino[4,3-a]indole (1)

1-Nitroso-2-naphthol copper salt (0.408 g, 1.0 mmol) and piperidine (0.425 g, 5.0 mmol) were added to 20 mL ethanol. The resulting mixture was stirred for 4 h at reflux. The mixture of 1-(2-Hydroxyethyl)-5-methoxy-2,3,3-trimethyl-3H-indolium Bromide (0.367 g, 1.8 mmol) and triethylamine (1 mL) in 20 mL ethanol after stirred for 30 min at room temperature was added to the solution, and stirred for 8 h at reflux. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1v/v) as the eluent to give light yellow solid **1** in 24% yield.

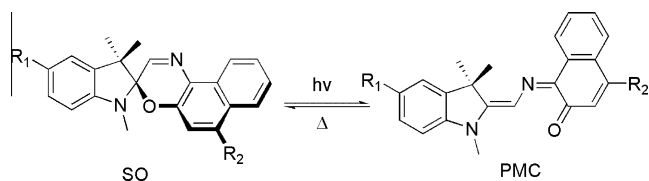
M.p. 202–204 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.40 (d, $J = 10.8$ Hz, 1H, Ar-H), 8.09–8.11 (m, 1H, Ar-H), 7.39–7.50 (m, 2H, Ar-H), 6.56–6.76 (m, 4H, Ar-H), 4.35–4.39 (m, 2H, O- CH_2), 3.66–3.96 (m, 5H, N- CH_2 , OCH_3), 3.02–3.03 (m, 4H, N(CH_2) $_2$), 1.83–1.84 (m, 4H, $\text{CH}_2(\text{CH}_2)_2$), 1.58–1.66 (m, 2H, $\text{CH}_2(\text{CH}_2)_2$) 1.31 (s, 3H, C- CH_3), 1.28 (3H, s, C- CH_3) ^{13}C NMR (CDCl_3 , 100 MHz) δ : 155.5, 152.2, 142.6, 139.9, 138.7, 130.6, 126.6, 125.3, 125.2, 123.8, 123.7, 122.5, 113.3, 111.6, 109.0, 105.9, 99.9, 67.0, 55.8, 54.8, 52.3, 44.8, 27.8, 26.7, 26.4, 24.4. IR (KBr); ν : 2935, 1635, 1587, 1498, 1458, 1280, 1257, 1236, 1217, 1155, 1128, 1051, 1033, 825, 771 cm^{-1} ; HRMS calcd for $\text{C}_{29}\text{H}_{31}\text{O}_3\text{N}_3$ $[\text{M}+\text{H}]^+$ 470.2444, Found $[\text{M}+\text{H}]^+$ 470.2435.

X-ray crystallography

By recrystallization from the mixture solvents (ethanol and trichloromethane) at room temperature, colorless single crystals were obtained for X-ray diffraction analysis. The diffraction measurements were made on a Rigaku Saturn 724 CCD diffractometer Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The data were collected at 113(2) K. Linear absorption coefficient 0.086 mm^{-1} . In the range of $1.99 < \theta < 27.91^\circ$. 30,258 integrated reflections were collected, reducing to a data set of 3191 unique with $R_{\text{int}} = 0.0494$, and completeness of data (to $\theta = 27.91^\circ$) of 99.6%. Data were collected and processed using Crystal Clear (Rigaku). An empirical absorption correction was applied using Crystal Clear (Rigaku). The structure was solved by direct methods with SHELXS-97 program [16]. Refinements were done by the full-matrix least-squares on F^2 with SHELXL-97 program [17]. The crystal structure and packing diagram were depicted using MERCURY [18]. All of the non-H atoms were refined anisotropically by full-matrix least-squares to give the final $R = 0.0387$, $wR = 0.0898$, ($w = 1/[\sigma^2(F_o^2) + (0.0589 - P)^2 + 0.0159P]$, where $P = (F_o^2 + 2F_c^2)/3$) with $(\Delta/\sigma)_{\text{max}} = 0.002$ and $S = 1.074$ by using the SHELXL program. All of the hydrogen atoms were placed by calculation geometry and took part in refinement. The corrections for absorption were multi-scan, $T_{\text{min}} = 0.9831$ and $T_{\text{max}} = 0.9898$. Selective crystal data for the title compound **1** are shown in Table 1.

Spectral measurements

The solutions of compound **1** in trichloromethane, carbontetrachloride and cyclohexane with the concentration of 1×10^{-4} mol L^{-1} were prepared. The UV-visible absorption spectra were measured at room temperature using a Shimadzu UV-2101PC spectrophotometer. The samples were irradiated with a 12 W ultraviolet lamp at 365 nm. The fatigue resistance was examined after 10-cycle irradiation of UV and visible lights.



Scheme 1. The structural interchange between the SO and PMC isomers.

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