

Alkali induced chromics and stable single crystal of opened-ring form of a new spirooxazine

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Abstract

Stable single crystal of the opened-ring form of a new spirooxazine was synthesized. Its structure was confirmed by X-ray crystallographic analysis. Its alkali induced chromism and thermochromism in the alkali medium were studied. A new kind of organic thermochromic paint indicating temperature having different chromogenic temperatures is made by this new spirooxazine in the presence of different solvents and different amines.

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1. Introduction

Photochromic organic compounds have widely been studied over the past decades because of their potential application in various photoactive devices such as optical memory, optical switches, displays and non-linear optics [1–5]. Spirooxazines (SO) are a type of well-known photochromic compounds that have been attracting much interest from the viewpoints of fundamental elucidation of photochemical reactions as well as from their potential applications to optical memories [6–12]. The photochromism of these molecules is due to the photocleavage of the spiro bond under UV irradiation, creating a deeply colored ring-opened photomerocyanine form (shown in Fig. 1) which absorbs in the visible spectral region and can be reverted back to the ring-closed form by visible-light irradiation

or heating. But, in past decades, spirooxazine's application in memory is highly restricted by the short lifetime of the colored photomerocyanine species which reverts thermally to the ring-closed colorless spirooxazine form with a reaction half-time of $1-10^3$ s and an apparent activation energy of 14–30 kcal/mol [12]. Many theoretical studies about the ring-closing reaction dynamics [12–14] have been made and various methods stabilizing the photomerocyanine form [15–18] have been developed. For example, Wirnsberger et al. [18] doped photochromic spirooxazine dyes into the mesostructured materials, which are excellent hosts for stabilizing the photomerocyanine form of the photochromic dyes. Such host/guest nanocomposites combine the high stability of the inorganic host framework with the diversity of the guest dopants, leading to versatile optical properties for applications in e.g. ultra-high density photochromic devices. Since a number of isomers exist for the photomerocyanines, molecular orbital calculation and NMR-NOE experiments had been done to estimate the most stable structure of spironaphthoxazine which was described in the quinoidal form (TTC structure

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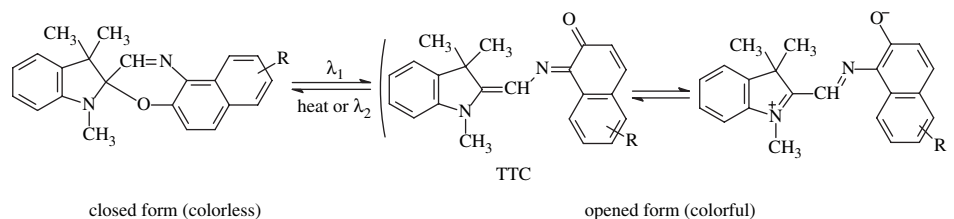


Fig. 1. Photochromism mechanism of a typical spironaphthoxazine.

shown in Fig. 1) [19]. From Fig. 1 we can understand that the poor thermal stability of the opened-ring form results from the exorbitant electronegative density of the oxygen atom on naphthalene ring. So the simplest method to improve the thermal stability of the opened-ring form of spironaphthoxazine should be one to reduce electronegative density of the oxygen atom by introducing electron-withdrawing groups or hetero atom to the naphthalene ring.

Pyridone derivatives are a kind of important heterocyclic compound [20]. There is not only nitrogen hetero atom, but also electron-withdrawing groups such as cyano group and carbonyl group on the rings. In this paper, we introduced a pyridone unit to synthesize a thermal stable opened-ring photomerocyanine form of spirooxazine (**Py-SO**) shown in Fig. 2 by reacting 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone with 1,3,3-trimethyl-2-methyleneindolenine. A stable single crystal of the opened-ring form of this new spirooxazine was obtained and its structure was confirmed by X-ray crystallographic analysis. To our best knowledge, it is the first example of stable single crystal for the opened-ring merocyanine form of spirooxazine derivatives. The tunable chromism and thermochromism in the alkali medium were observed for this new spirooxazine, with which a new kind of organic thermochromic ink indicating chromomeric temperature is made in the presence of different solvents and different amines.

2. Experimental

IR spectra of the products were carried out on a Nicolet Magna-IR550 instrument using KBr tabulating. ^1H NMR spectra were measured on Brüker AVANCE 500 at 500 MHz in deuterium solvent with TMS as an internal reference. EI mass spectra (70 eV)

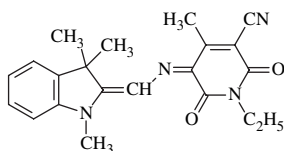


Fig. 2. Structure of **Py-SO** studied in this work.

were recorded on a HP5989A spectrometer. UV–vis absorption spectra were performed on a Varian Cray500 spectrophotometer. Fluorescence spectra were recorded on a Varian Cray Eclipse Fluorescence Spectrophotometer.

2.1. Synthesis of 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone

Two grams (0.05 mol) NaOH and 8.9 g (0.05 mol) 1-ethyl-3-cyano-6-hydroxyl-4-methyl-2-pyridone were dissolved in 85 ml water. The solution was cooled to 0–5 °C in ice-salt bath, and then 3.55 g (0.05 mol) NaNO_2 was added into it with stirring well. Sulfuric acid solution (containing 6.57 g sulfuric acid and 11.4 g ice-water) was stirred into the solution. During this procedure, the temperature of the mixture was maintained within 0–5 °C. Stir further for 1 h. Green solid was collected by filtration and washed with 200 ml water. The solid was recrystallized with ethanol to give 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone in 90% yield, mp 144–146 °C.

2.2. Synthesis of target product **Py-SO**

A mixture of 1,3,3-trimethyl-2-methyleneindolenine (3.46 g, 0.02 mol) and 1-ethyl-3-cyano-6-hydroxyl-4-methyl-5-nitroso-2-pyridone (4.14 g, 0.02 mol) in absolute ethanol (100 ml) was refluxed for 2 h with N_2 as protection. The mixture was cooled to room temperature. The precipitate solid was filtered and recrystallized with ethanol to give title compound **Py-SO** in 92% yield, mp 264–267 °C. ^1H NMR (CDCl_3) δ 1.23 (t, 3H, $J = 7.10, 7.08$ Hz, $-\text{CH}_2-\text{CH}_3$), 2.57 (s, 6H, $-\text{C}(\text{CH}_3)_2$), 3.76 (s, 3H, $-\text{N}-\text{CH}_3$), 4.04 (m, 2H, $-\text{CH}_2-\text{CH}_3$), 7.21 (d, 1H, $J = 7.72$ Hz, Ar-H), 7.34 (t, 1H, $J = 7.49, 7.11$ Hz, Ar-H), 7.47 (m, 2H, Ar-H), 9.65 (s, 1H, $-\text{CH}=\text{N}-$). MS m/z (rel. int.%) 363 (M^+ , 23.73), 362 (73.76), 347 (13.24), 160 (7.95), 159 (100.00), 145 (7.69), 144 (22.53). IR (cm^{-1}) 3450, 2210, 1658, 1615, 1263.

2.3. X-ray crystallographic analysis

Preliminary experiment and data collection for X-ray crystal structure determination were performed on

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