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Crystalline-state photochromism and thermochromism of new spiroxazine

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Abstract

New spiroxazine **7** carrying a long alkyl chain was prepared by condensation of spiroxazine **5** with glutaric anhydride. The first example of solid-state photochromism and thermochromism in spiroxazine **7** is reported.

Keywords: Crystalline-state photochromism; Thermochromism; Spiroxazine

1. Introduction

A photochromic compound is characterized by its ability to undergo a reversible colour change. Interest in the photochromism of organic materials began to increase substantially around 1940. The principal studies of photochromic compounds involved acquiring an insight into mechanisms of the photoprocesses, determining the structures of the uncoloured form and the coloured form, and developing synthetic methods. The development of time-resolved or flash spectroscopy and, more recently, the use of laser photophysical means opened new approaches to study of the excited states and transient species involved in the photoreactivity of photochromic molecules.

Recently, photochromic materials have gained much attention, and they now constitute an active research area because of their tremendous importance in biological phenomena and in their potential applications in the areas of linear and nonlinear optics [1].

A number of organic compounds undergo reversible colour changes by the alternation of the molecular structure with temperature. The reversible colour change observed for a variety of compounds with temperature variation is known as thermochromism.

In recent years, photochromic and thermochromic spiropyrans and spiroxazines have been receiving considerable attention, due to their potentional application in many new technologies,

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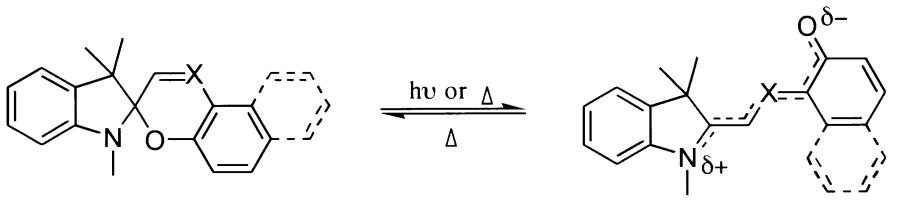


colorless form colored form

X = CH : spiropyran

X = N : spiroxazine

such as data recording and storage, optical switching, displays, and nonlinear optics [2,3].

Although spiroheterocyclic compounds have attracted significant attention because of their potential use, they still await major commercial exploitation. One of the prime reasons for the lack of industrial applications for photo- and thermochromic materials, particularly organic compounds, is their poor durability. Although the thermo- and photochromism of spiropyran has been extensively studied [4–7], only little work has been carried out on spironaphthoxazine dyes. These two classes of compounds are similar in many respects, but the replacement of the benzopyran ring by a naphthoxaine ring, which results in spironaphthoxzine, greatly improves resistance to prolonged UV irradiation, which confers greatly commercial importance [8].

We have previously reported on the synthesis, photochromic properties and solvatochromic properties of spironaphthoxazines [9–11]. Among the great number of photochromic spiroxaines reported only a few are known to show crystalline state photochromism [12].

We report herein a new spiroxazine that exhibit photochromism and thermochromism both in solution and in the crystalline state.

2. Experimental

2.1. Characterization of products

Melting point was determined using a Electrothermal IA 900 and are uncorrected. A multichannel photodiode detector (MCPD, Otsuka Electronics Co., Japan) was used to obtain visible absorption spectra of spiroxazine in solution and crystalline state. A light source, I_2 lamp, was projected and light collected using a Y-type optical fiber. Elemental analysis were recorded on a Carlo Elba model 1106 analyzer. ^{1}H NMR spectra was recorded in $CDCl_3$ using a Varian Inova 400 MHz FT–NMR spectrometer using TMS as internal standard.

2.2. Synthesis of spiroxazines and intermediate

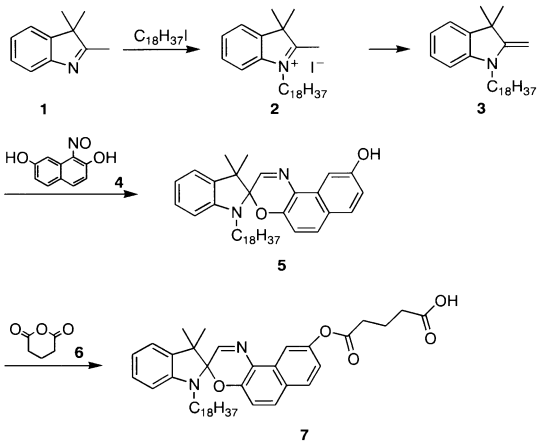
2.2.1. Intermediate *2*, *3*

2,3,3-Trimethylindolenine **1** (4 g, 25.12 mmol) and 1-iodooctadecane (9.6 g, 25.23 mmol) were reflux for 40 h in 20 ml of 2-butanone. The solvent was removed in vacuo and then 40 ml of ethanol was added to the reaction mixture. The precipitated solid was filtered and dried to give **2** in 66.4% yield. Compound **2** (9 g, 16.68 mmol) thus obtained was added to 25 ml of water and 9 ml of chloroform (Scheme 1).

To the solution was added dropwise 10.3 ml of 50% aqueous NaOH solution, and the reaction mixture was stirred for 2 h at room temperature, which was then extracted using chloroform. The solution was dried with anhydrous magnesium sulfate and concentrated under reduced pressure to give **3** in 90.3% yield.

2.2.2. Spiroxazine dye *5*

A mixture of **3** (6.2 g, 15.06 mmol) and l-nitroso-2,7-dihydroxynaphthalene 4 (2.8 g, 15.06 mmol) in absolute ethanol (150 ml) was stirred



Scheme 1.

under reflux for 4 h. The solvent was distilled off under reduced pressure and then 30 ml of ethyl acetate was added to the reaction mixture. The precipitated solid was filtered and dried to give **5** in 41.4% yield, mp 100–107 °C. ^{1}H NMR ($CDCl_3$): δ 0.87 (*t*, 3H, $J=6.8$ Hz), 1.20 (*m*, 2H), 1.25 (*m*, 30H), 1.32 (*s*, 3H), 1.33 (*s*, 3H), 3.18 (*t*, 2H, $J=7.1$ Hz), 6.58 (*d*, 1H, $J=7.8$ Hz), 6.81 (*d*, 1H, $J=8.9$ Hz), 6.86 (*t*, 1H), 7.00 (*d*, 1H, $J=8.6$ Hz), 7.05 (*d*, 1H), 7.19 (*t*, 1H), 7.56 (*d*, 1H, $J=8.8$ Hz), 7.64 (*d*, 1H, $J=8.8$ Hz), 7.68 (*s*, 1H), 7.81 (*s*, 1H), anal. calcd for $C_{39}H_{54}N_2O_2$: C, 80.37; H, 9.34; N, 4.81. Found: C, 81.61; H, 9.65; N, 4.59.

2.2.3. Spiroxazine dye 7

Spiroxazine dye **5** (3 g, 5.15 mmol), glutaric anhydride **6** (0.59 g, 5.15 mmol) and triethyl amine (0.52 g, 5.15 mmol) in CH_2Cl_2 (20 ml) was refluxed for 8 h. The reaction mixture was extracted with ethyl acetate and dried with anhydrous magnesium sulfate and concentrated under reduced pressure and then 30 ml of ethyl acetate was added to the reaction mixture. The precipitated solid was filtered and dried to give **7** in 39% yield, mp 87–90 °C. ^{1}H NMR ($CDCl_3$): δ 0.87 (*t*, 3H, $J=6.8$ Hz), 1.21 (*m*, 2H, $J=8.1$ Hz), 1.24 (*m*, 30H), 1.32 (*s*, 3H), 1.33 (*s*, 3H), 2.14 (*m*, 2H, $J=7.2$ Hz), 2.58 (*t*, 2H, $J=7.2$ Hz), 2.74 (*t*, 2H, $J=7.3$ Hz), 3.16 (*t*, 2H, $J=4.8$ Hz), 6.58 (*d*, 1H, $J=7.8$ Hz), 6.87 (*t*, 1H), 6.96 (*d*, 1H, $J=8.8$ Hz), 7.05 (*d*, 1H), 7.12 (*d*, 1H, $J=8.8$ Hz), 7.19 (*t*, 1H), 7.64 (*d*, 1H, $J=8.8$ Hz), 7.70 (*s*, 1H), 7.74 (*d*, 1H, $J=8.8$ Hz), 8.20 (*s*, 1H), anal. calcd for $C_{44}H_{60}N_2O_5$: C, 75.83; H, 8.68; N, 4.02. Found: C, 75.33; H, 8.89; N, 3.91.

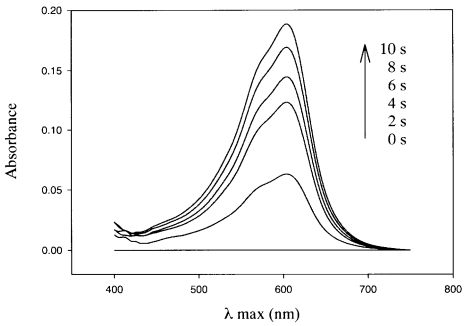


Fig. 1. Visible spectral changes of spiroxazine **7** in toluene solution (2.68×10^{-2} M, room temperature) upon UV irradia-

3. Results and discussion

3.1. Photochromism

Photochromism in spiroxazine compounds generally involves the UV-induced dissociation of the spiro C–O bond, from the oxazine ring, to form a planar structure. This is commonly referred to as the photomerocyanine product. The photomerocyanine is usually less stable and returns to the closed form both thermally and photochemically [1]. Electronic absorption spectral changes of spiroxazine **7** upon UV irradiation in toluene are depicted in Fig. 1.

The original spectral pattern is reversibly recovered within 10 s. The new band is ascribable to the generation of the open merocyanine form from the closed spiro form. Spectra measured after UV irradiation are at any time proportional to each other in the visible region, indicating that only one species is formed. This allowed the absorption to be monitored at a λ_{max} (605 nm) as a function of time to obtain thermal colour fading rate (k).

Tomioka has examined the thermal decolouration rate for photochromic spiropyran derivatives using first-order kinetics [13]. The kinetic equation approach to the open merocyanine to closed spiro form via first-order reaction in the present case, is given by

$$A_t - A_\infty = A_i \cdot \exp(-kt) \quad (1)$$

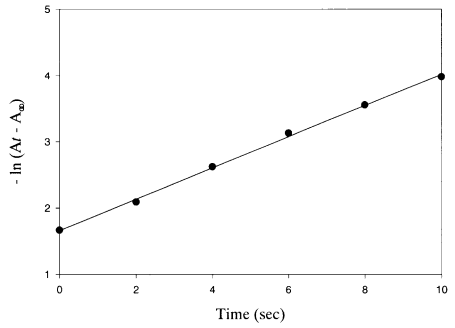


Fig. 2. Plot of $-\ln(A_t - A_\infty)$ as a function of time according to Eq. (1) for the decolouration of spiroxazine **7**.

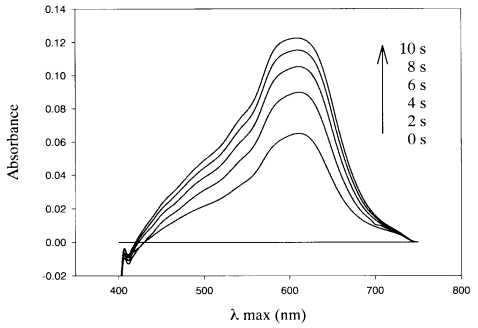


Fig. 3. Visible spectral changes of spiroxazine **7** in crystalline state.

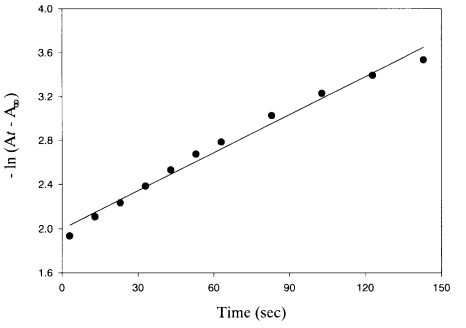


Fig. 4. Plot of $-\ln(A_i - A_\infty)$ as a function of time according to Eq. (1) for the decolouration of crystalline-state spiroxazine **7**.

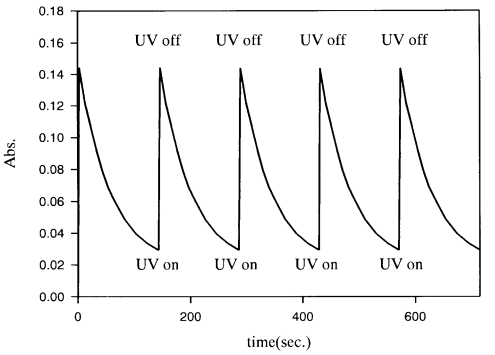


Fig. 5. Absorbance changes at 605 nm of crystalline-state spiroxazine **7** following periodic UV illumination.

where A_i is the absorbance at 605 nm, and A_t is the absorbance at 605 nm at any time t after UV irradiation. A_∞ and k refer to absorbance at 605 nm after 1 h and first-order colour changing rate constant, respectively. In the thermal colour changing process, the kinetic analysis predicts the logarithm of the difference between A_∞ and A_t at time t to be linear with time, the slope giving the decolouration rate constant, k. First-order plots according to Eq. (1) for spiroxazine dye **7** is shown in Fig. 2. The colour changing rate constant $k = 23.5 \times 10^{-2}\ s^{-1}$ was obtained from the slope.

Irradiation of a crystalline sample of spiroxazine **7** was carried out using an ultra-thin pressed pellet. The UV–vis absorption spectra after different irradiation times are shown in Fig. 3.

Upon UV irradiation a broad absorption band appeared at around 610 nm and continuously increased, depending on the irradiation time. When the sample was left in the dark at room temperature after irradiation, the absorbance at 610 nm was decreased slowly. The reason why falling time is longer than rising time is explained that quantum efficiency of the reversal process is lower than that of forward case like a previously reported study [14].

The spectral changed observed in the visible region for crystalline state spiroxazine **7** is similar to that of solution state. Good first-order kinetics was obtained when the rate of decolouration of the spiroxazine **7** was measured in crystalline state: $k = 1.15 \times 10^{-2}\ s^{-1}$ (Fig. 4).

The first-order decolouration rate constant in the crystalline state is smaller than that of in solution, which indicates that open-to-closure occurs more readily in solution than in the crystalline state. This photochrome also exhibited a fairly good reversibility, as can be seen from Fig. 5, where consecutive colouration-decolouration cycles are shown.

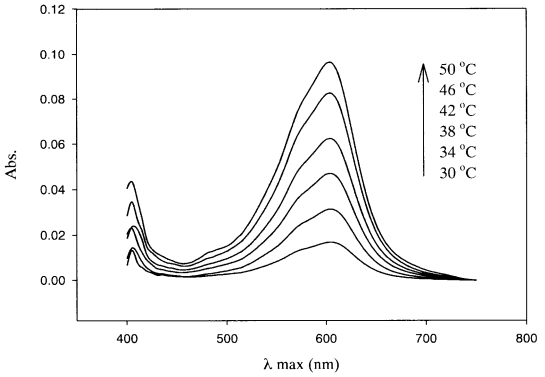


Fig. 6. Optical absorbance of spiroxazine **7** at various temperatures in the region of the thermochromic band in chloroform.

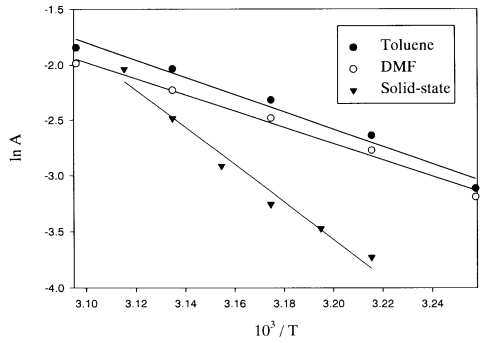


Fig. 7. Data for thermal equilibrium treated according to the van't Hoff equation.

The reason for the crystalline state photochromism of spiroxazine **7** could be attributed to the presence of the long alkyl chains which provide more space compared to the other spiroxazines.

3.2. Thermochromism

The thermochromism of spiropyrans, discovered in 1926, has been extensively studied. However, thermochromic properties of spiroxazines have been more recently reported [15]. The nature of the coloured form of spiropyrans and spiroxazines in solution has been discussed widely. The spectroscopic identity of the thermochromic and photochromic transients was first noted by Hirshberg and Fisher [16]. It is generally assumed that a photo- and thermo-sensitive equilibrium exists between the spiro form and a planar, coloured form resulting from scission of the bond between

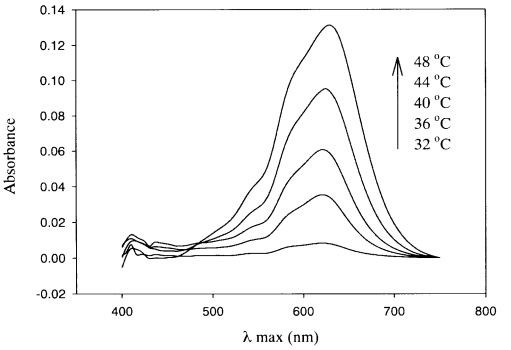


Fig. 8. Optical absorbance of crystalline-state spiroxazine **7** at various temperatures in the region of the thermochromic band.

spiro carbon and pyran/oxazine oxygen. Spiroxazine **7** shows thermochromism; that is, there is a measurable concentration of merocyanine in thermal equilibrium with spiro form. Fig. 6 shows the absorption spectral changes of the spiroxazine **7** at different temperatures.

The absorption intensity increased as the temperature increased, that is, the spiroxazine **7** exhibited thermochromic property in solution.

The enthalpy of reaction could be evaluated by measuring the absorbance of the open form at several temperatures, according to the van't Hoff equation, $\mathrm{d}\ln K/d(1/T) = \mathrm{d}\ln A/d(1/T) = -\Delta H/R$. Plots of ln A vs. $1/T$ are shown in Fig. 7.

In the above Eq. (1), the slope of a straight line of ln A versus $1/T$ equals $-\Delta H/R$. The smaller ΔH value (61.08 kJ/mol) in DMF than in toluene (65.03 kJ/mol) is responsible for the stabilization of open merocyanine form in the polar DMF solvent.

The UV–vis absorption spectra of the crystalline sample are shown in Fig. 8 at different temperatures.

As the temperature increased, the colourless crystal turned blue. The blue colour of the crystal is due to the formation of merocyanine. The thermally reversible crystalline thermochromic material are potentially applicable to thermal switches. This is the first example of crystalline state thermochromism of spiroxazine dye. A linear dependence of ln A vs. $1/T$ yielded the ΔH value of 132 kJ/mol.

The large ΔH value in crystalline state thermochromism than that of solution state indicates that the energy difference between the spiro form and open merocyanine form in solid state

thermochromism is larger than that of solution state thermochromism.

Acknowledgements

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