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Acidichromic effects in spiro(1,3,3-trimethylindolo-2,3′-naphth[1,2-*b*]-1,4-oxazine), a photochromic compound

I. Absorption characteristics

X.D. Sun [a], M.G. Fan [b], X.J. Meng [b], E.T. Knobbe [a,*]

[a] *Department of Chemistry and the University Center for Laser Research, Oklahoma State University, Stillwater, OK 74078-0447, USA*

[b] *Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, People's Republic of China*

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Abstract

Acidichromic and photochromic effects in alcoholic solutions of spiro(1,3,3-trimethylindolo-2,3′-naphth[1,2-*b*]-1,4-oxazine) are described. First-order, thermally-initiated decay kinetics associated with relaxation of the merocyanine form under acidic conditions are reported. A model for acidichromic and photochromic processes in these systems has been proposed. Preliminary results indicate that spirooxazine compounds are potentially useful in device applications such as pH sensors.

Keywords: Acidichromism; Photochromism; Spirooxazine

1. Introduction

Photochromism in organic systems is a phenomenon entailing the reversible change of a selected chemical species from one molecular form to another; the transformation is accompanied by a readily discernible change in the optical absorption spectrum between two states having distinguishable absorption spectra. Structural transformation is induced, in at least one direction, by light energy. Relaxation back to the initial state is often thermally activated. The first study of photochromic change was reported by Fritsche in 1867 [1]. In 1871, the first systematic study of spiropyrans was published by Houston [2]. However, the term "photochromism" did not appear in the literature until it was suggested by Hirshberg in 1950 [3].

The spiropyrans represent a family of photochromic and thermochromic compounds which have been widely studied over the past four decades [4–6]. Recently a new class of photochromic compound, the spirooxazines, has been the subject of renewed interest in the field. The spirooxazines have been found to be resistant to cycling fatigue, a characteristic which makes them especially attractive from an application's perspective.

The authors have investigated photochromic effects in alcoholic solutions containing spiro(1,3,3-trimethylindolo-2,3′-naphth[1,2-*b*]-1,4-oxazine) (also referred to as SP1 hereinafter). Among our findings, we have observed that SP1 is quite sensitive to solution pH. When a neutral alcoholic SP1 solution is made acidic by addition of HCl, the absorption, luminescence and photochromic characteristics are substantially changed. The authors have coined the phrase "acidichromic" to indicate such a phenomenon, wherein the spectral characteristics of a photochromic species are reversibly changed by pH variance. We believe that research in the area of acidichromic media will become quite active, as the absorption and emission characteristics of such chromophoric species may be tuned by adjusting the pH.

Photochromism in spirooxazine 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 (or PMC) product. PMC is reported to be a mixture of at least four structurally distinguishable isomers (e.g. cis and trans conformations) in common solvents [7]. The normal chemical structure of the spiro(1,3,3-trimethylindolo-2,3′-naphth[1,2-*b*]-1,4-oxazine), and the corresponding UV-induced photomerocyanine form, are shown in Scheme 1. Results described herein include pH-dependent acidichromic and photochromic processes in solution. Discussion of observed acidichromic photoproduct kinetic decay characteristics is included.

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* Corresponding author.

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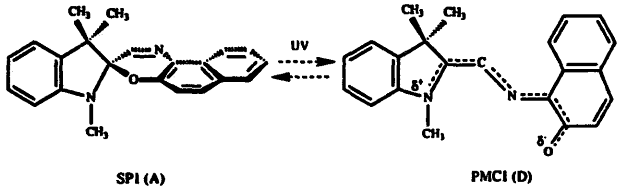


Scheme 1. Chemical structure of SP1 and the corresponding UV-induced photomerocyanine form.

2. Experimental

SP1 was synthesized from 2-methylene-1,3,3-trimethylindoline and 1-nitroso-2-naphthol; the synthetic approach has been fully described elsewhere [8]. SP1 solutions for acidichromic studies were prepared by dissolving SP1 in anhydrous reagent grade isopropanol (Fisher Scientific Company). Solution pH, as determined using pH paper (EM Sciences, ±0.5 pH units), was adjusted by dropwise addition of 0.4 M HCl solution from deionized and distilled water. The UV irradiation source was a B-100SP 160-W (Fisher Scientific Company) UV Lamp with a specified intensity of 11.6 mW cm^{-2}. Absorbance spectra were determined using a Cary 5E spectrophotometer (2.0 nm spectral band pass) and 1.0×10^{-4} M SP1 solutions in quartz cuvettes having 1 cm pathlength. All spectral measurements were conducted in the dark at room temperature.

3. Results and discussion

Fig. 1 shows the acidichromic effects in a 0.1 mM SP1 isopropanol solution. Curve A represents the absorption spectrum of SP1 in pure isopropanol solution. An intense peak centered at 320 nm and exhibiting a shoulder at 350 nm was observed. This absorption band structure was found to be comparatively insensitive to the presence of water, as isopropyl alcohol solutions containing SP1 and up to 20 vol.% H_2O were found to have absorption spectra which were indiscernible from that shown in Fig. 1. Upon acidification by addition of HCl, the optical density of the region below 360 nm decreased noticeably. The solution pH, as determined by pH paper, was lowered from values of 7 (curve A) to 6 (curve H) and 4 (curve B). Under acidic conditions, a new absorption band appeared in the visible region ($\lambda_{max}=430$ nm) and grew in intensity as the pH was lowered. Over this pH range, an isosbestic point was observed, indicating that only two distinct species are involved in the acidichromic process associated with curves A, H and B in Fig. 1. The indicated acidichromic reaction is hypothesized to result in a complex of SP1 and HCl according to:

$$SP1+HCl \rightarrow SP1\cdot HCl \qquad (1)$$

where SP1 · HCl represents the acidichromic product. The spectrum of SP1 · HCl is indicated by curve B in Fig. 1.

Upon addition of more acid (pH lowered to 3; curve J of Fig. 1), the absorption curve exhibited a departure from the isosbestic behavior found at higher pH values. A pH value of 3 is consistent with an HCl concentration which is tenfold that of SP1 in the alcoholic solution. This result indicates the formation of one or more additional species in the solution under such conditions. It is speculated that SP1 may form complexes with more than one hydrogen chloride equivalent.

Fig. 2 represents the absorption characteristics of four readily distinguished species. Curves A and B are associated with the absorption spectrum of SP1 in anhydrous isopropanol and acidified (pH 4) alcoholic solutions, respectively (also shown in Fig. 1). Irradiation of the acidichromic product (B) with UV light yields the absorption spectrum indicated as curve C in Fig. 2. Curve D is taken from the work by Bohne et al., indicating the corresponding absorption band of PMC1 (species D, shown in Scheme 1), which reportedly peaks near 600 nm in acetonitrile [9]. The photochromic product (C) has a new absorption band centered at 526 nm, a hypsochromic shift of some 74 nm compared with curve D. Thus photochromic effects which are observed in SP1 solutions are also observed for solution containing the acidichromic product, SP1 · HCl. Photochromism in the SP1 · HCl solutions was found to be completely reversible.

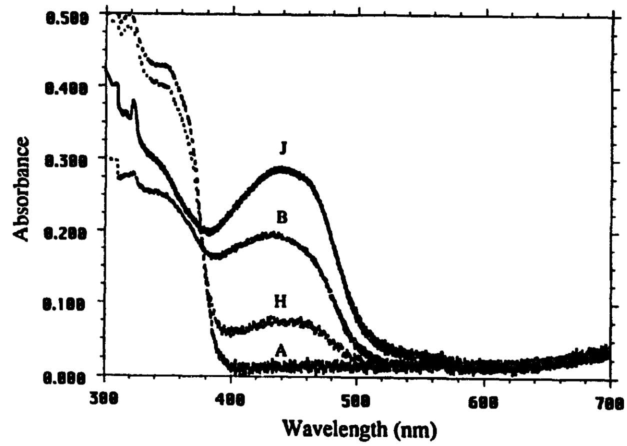


Fig. 1. Absorption spectra of alcoholic spirooxazine solutions (1.0×10^{-4} M) as a function of pH. (A) pH = 7; (H) pH = 6; (B) pH = 4; (J) pH = 3.

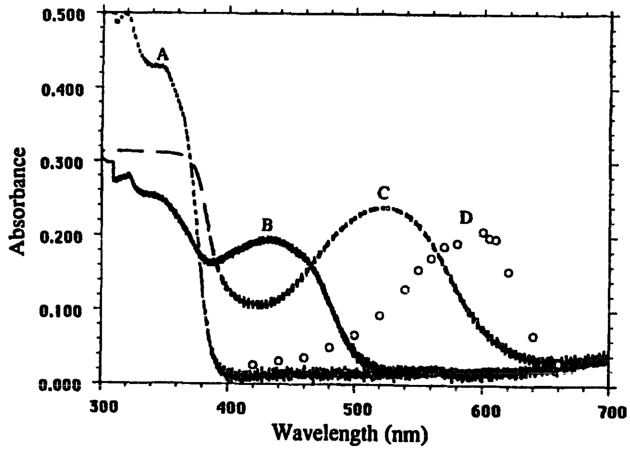
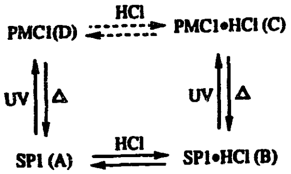


Fig. 2. Absorption spectra of alcoholic SP1 solutions. (A) pH = 7; (B) acidichromic product SP1 · HCl formed at pH = 4; (C) photochromic product of SP1 · HCl, PMC1 · HCl; (D) photochromic product of SP1 in acetonitrile, data from Ref. [9].

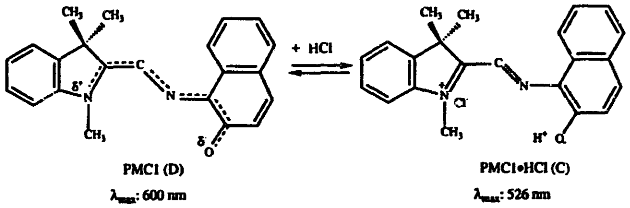
A proposed model given in Scheme 2 suggests the chemical species associated with the observed acidichromic and photochromic processes. The transformation of SP1 (A) to SP1·HCl (B) represents the acidichromic process which is evidenced by the spectral shifts observed in Fig. 1. Conversion of the SP1·HCl (B) form to the photomerocyanine complex, PMC1·HCl (C), is the UV-induced photochromic process evidenced in Fig. 2. It is known that PMC1 (D), the photochromic product of SP1 (A) generated by UV irradiation under neutral conditions, is a blue species with a conformational lifetime of approximately 0.5 s in acetonitrile [9]. Because PMC1 (D) is a comparatively short-lived species, it is difficult to observe complexation transformation between PMC1 (D) and PMC1·HCl (C). PMC1 may have acidichromic properties similar to SP1, as indicated by the dashed arrow in Scheme 2, although these have not been directly observed.

Although the structures of SP1·HCl (B) and PMC1·HCl (C) are not reported, it is possible to conjecture on conformational changes induced by complexation through interpretation of spectroscopic data. SP1 (A) is known to have a twist arrangement between the two ring systems [9]. In the absence of substantial molecular rearrangements, bathochromic shifts such as the one observed in Fig. 1 (curves A and B) must be associated with the formation of a more planar molecular conformation, resulting in resonance forms having increased effective conjugation lengths. Conversely, PMC1·HCl (C) was found to exhibit a large hypsochromic shift compared to the spectrum reported for the PMC1 (D) form. This result may be interpreted as follows. In PMC1 (D), the indolino-nitrogen is a good electron donor, while the oxygen atom bound to the naphthyl ring is a good electron-withdrawing species. PMC1 (D) may exist as a planar, fully conjugated structure having an extensive delocalized π-electron system which results from the donor–acceptor resonance structure shown in Scheme 3. When hydrogen chloride begins to complex with the conjugated system, the donor–acceptor system is destroyed through the formation of an internal salt, PMC1·HCl (structure C, Scheme 3). The loss of the donor–acceptor system is associated with reduced π-system delocalization and a concomitant hypsochromic-shift in the absorption spectrum for the PMC1·HCl (C) with respect to PMC1 (D).

The photochromic product PMC1·HCl (C), which is generated upon UV excitation of SP1·HCl (B), spontaneously decays back to the SP1·HCl (B) form at room temperature. It is postulated that this transformation is thermally activated. The decay curve from the PMC1·HCl (C) to the SP1·HCl (B) form is shown in Fig. 3. The change in optical density (absorption $\lambda = 526$ nm) was measured as a function of time immediately following a 2 min irradiation exposure at 365 nm (estimated to be 14 mJ cm^{-2}). A plot of the natural logarithm of relative absorbance (A/A_0) versus decay time was found to be of first order, with a correlation coefficient of 0.999 (over nearly three lifetime periods as indicated in the Fig. 3 inset). The thermally-induced relaxation lifetime of the acidichromic product (C) was found to be 115 s. Thus, the HCl complex, PMC1·HCl (C), was found to have a much longer conformational lifetime (by more than two orders of magnitude) than that of the free PMC1 form, which has been reported to be about 0.5 s [9]. HCl complex-induced acidichromism, therefore, is noted to have unique effects on UV photoproduct lifetimes. Such changes are of potential interest in various device applications, such as optical information storage and/or opto-chemical transducers.



Scheme 2. Proposed transformation among the A, B, C and D forms.



Scheme 3. Proposed acidichromic process of the photomerocyanine form.

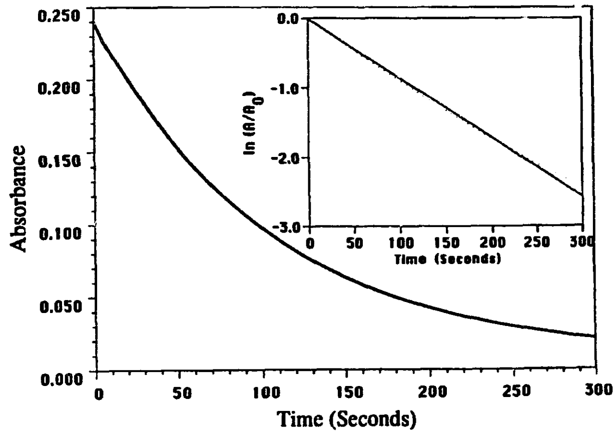


Fig. 3. Time evolution of alcoholic SP1 solution absorbance at 526 nm, (pH = 4), following UV irradiation. Inset: $\ln(A/A_0)$, versus decay time ($\lambda = 526$ nm); (· · ·) actual data; (———) single exponential fit.

4. Conclusion

Acidichromic effects in alcoholic spirooxazine solutions have been investigated. Spirooxazine (SP1) and its acidichromic product (SP1·HCl) exhibit dramatically different spectral characteristics; a new absorption peak at 430 nm for SP1·HCl was observed. In addition, the absorption band of PMC1·HCl was found to have undergone a hypsochromic shift, by 74 nm, with respect to the peak reported for PMC1 in acetonitrile. This hypsochromic shift is hypothesized to be due to changes in the donor–acceptor character of the PMC1 form, resulting in a perturbation to the conjugated π-electron system of photomerocyanine. Thermally-initiated relaxation kinetics of PMC1 · HCl to SP1 · HCl were found to be first order at room temperature, with a computed relaxation time of 115 s compared to approximately 0.5 s for the PMC1 form.

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