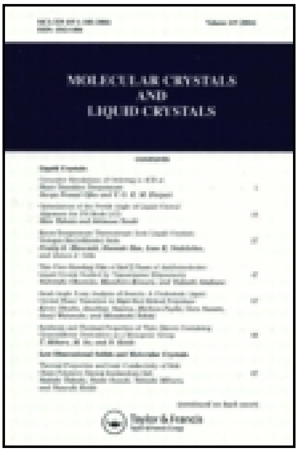

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‘ACIDICHROMICS’ of Photochromic Spirooxazines

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"ACIDICHROMICS" OF PHOTOCHROMIC SPIROOXAZINES

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Abstract Acidichromism of four photochromic spirooxazine compounds (SP) were investigated systematically. When hydroxyl group is introduced on the naphtho ring of spirooxazine, the spirooxazine compounds are found to have acidichromic properties in both acidic and basic solutions. Substituent effect on the absorption maximum of acidichromic products has been discussed. A comprehensive discussion of acidichromic, photochromic and thermochromic processes is included.

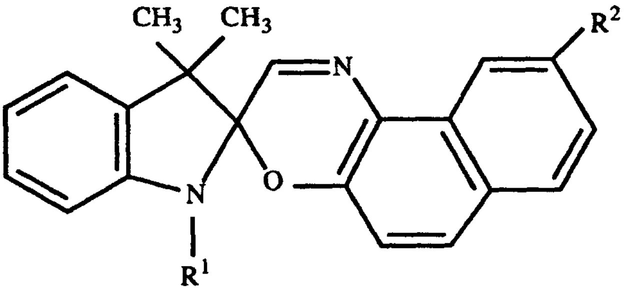
INTRODUCTION

Photochromism in organic molecules, which involves the switching between two conformational states of a system by optical means, has long been of interest from both theoretical and practical viewpoints.[1-7] The spirooxazines, a family of photochromic and thermochromic compounds, have been found to be resistant to cycling fatigue, a characteristic which makes them especially attractive from the perspective of device applications.

In 1993, Rys *et al.*[8] studied light-induced changes associated with molecular charge distribution in spironaphthoxazine as a function of pH in buffered solutions. They found that the absorption spectra of protonated spironaphthoxazine were shifted to shorter wavelengths when the solution pH was decreased from 4.52 to 1.28. They concluded that protonation occurred at the nitrogen site of the indoline moiety. Recently, we investigated photochromic effects in alcoholic solutions containing spiro(1,3,3-trimethylindolo-2,3'-naphth[1,2-*b*]-1,4-oxazine)[1,2] and found that when hydrogen chloride was added into an isopropanol solution of SP, a new absorption band resulted in the blue portion of the visible spectrum. We coined the phrase "acidichromic" to indicate such a phenomenon, wherein the spectral characteristics of a photochromic species are reversibly changed by varying the pH.

Current research is focused on achieving a better understanding of the mechanism of acidichromic behavior through systematic study of spirooxazine compounds and the effects of moiety substitution, solvent polarity and pH dependence on absorption characteristics. Discussion of the potential mechanisms associated with acidichromic, photochromic and thermochromic reactions of various spirooxazine compound is included.

Title compounds are shown as follows. The abbreviated names are simply given as SP1, SP2, SP3 and SP4, respectively, according to the R^1 and R^2 substituents as indicated.



SP1: $R^1 = CH_3$, $R^2 = H$;
SP2: $R^1 = CH_3$, $R^2 = OCH_3$;
SP3: $R^1 = CH_3$, $R^2 = OH$;
SP4: $R^1 = C_8H_{37}$, $R^2 = OH$.

Structure 1

EXPERIMENTAL

Title compounds SP1, SP2, SP3 and SP4 were synthesized using modified methods according to literature preparations.[9] The 365 nm light was a low pressure mercury lamp. All of the solvents were purified before use. Absorption spectra were recorded on Hitachi-557 spectrometer. All of absorption measurements were carried out in the dark at room temperature.

RESULTS AND DISCUSSION

1. pH Dependent of Absorption Spectra

In earlier studies,[1,2] the authors noted that addition of HCl into an isopropanol solution of SP1 and SP2 gave rise to a new absorption band centered at 436 nm in the case of SP1 solute, and 460 nm in the case of SP2). In each case, the absorption intensity of the new peak was found to gradually increase with HCl addition. Subsequent measurements have shown that SP3 and SP4 exhibit inherently comparable behavior, with the onset of an HCl-induced absorption band in isopropanol solution centered around 490 nm. By analogous reasoning to the ideas previously described[1,2], we have assigned the new peaks as the complex of SP3 and SP4 with HCl (*i.e.* SP3•HCl and SP4•HCl).

SP3 and SP4 each have a hydroxyl group attached at the 9'-position of naphthooxazine moiety, creating a β-naphthol (SPOH) functionality which is commonly known to behave as a weak acid. When isopropanol solutions of SP3 and SP4 were made basic by addition of sodium hydroxide, new absorption bands centered at 404 and 405 nm, respectively, were found to result (see Figure 1 for SP3 results; SP4 similar). Base-induced products formed in the isopropanol solution are proposed to have a salt-like structure of the type SPO^-Na^+. It should be noted that the postulated SPO^-Na^+ complex, which is formed in basic solution, is not very stable. The intensity of the absorption bands centered at 404 and 405 nm were found to decrease slowly when solutions were stored in the dark.

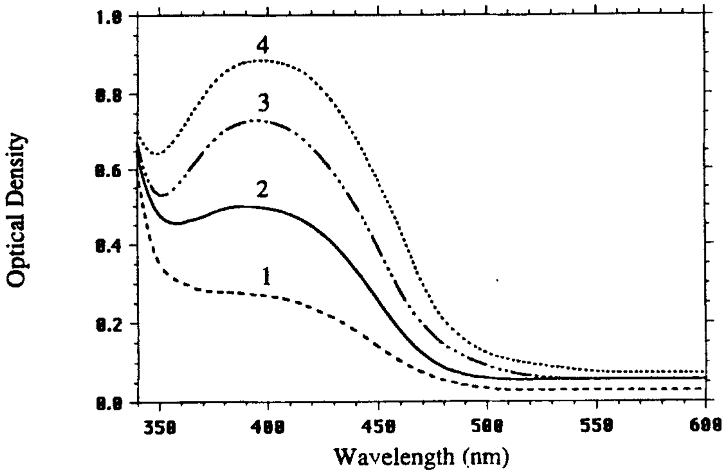


Figure 1. The absorption changes of SP3 in basic isopropanol solutions at low (curve 1, SP3: NaOH = 3.0), moderate (curves 2 and 3, SP3: NaOH = 1.5 and 1.0), and high (curve 4, SP3: NaOH = 0.6) sodium hydroxide concentrations.

The acid and base-induced peaks were found to be completely reversible. When sodium hydroxide was added into the acidic solution containing SP3•HCl, the absorption band centered at 490 nm gradually disappeared. This is consistent with regeneration of SP3 in the alcoholic solution. Addition of sodium hydroxide in excess of HCl equivalence gave rise to the 404 nm absorption band which is characteristic of the base-induced SPO$^-$Na$^+$ complex. Conversely, when hydrogen chloride was added into basic solution, the 404 nm band was eliminated and a 490 nm peak was subsequently induced by excess amount of HCl.

2. Photochromic Character of the Acidichromic Compounds

Photochromism of acidichromic compounds of SP1 and SP2 has been previously reported.[1-2] As discussed in Section 1, the acidichromic products associated with SP3 and SP4 compounds are readily distinguishable in both acidic and basic solutions. SP1 and SP2, by comparison, did not show base-induced chromophoric modifications.

450 nm irradiation of the acidichromic product (SP3•HCl) in isopropanol leads to a smooth decrease in absorption intensity of the 490 nm peak, as shown in Figure 2. There was a concomitant increase in absorption intensity at 340 nm. The increasing 340 nm band is consistent with elevated activities of the free SP3 form. Thus, UV-irradiation provides a secondary path for formation of SP3 from SP3•HCl.

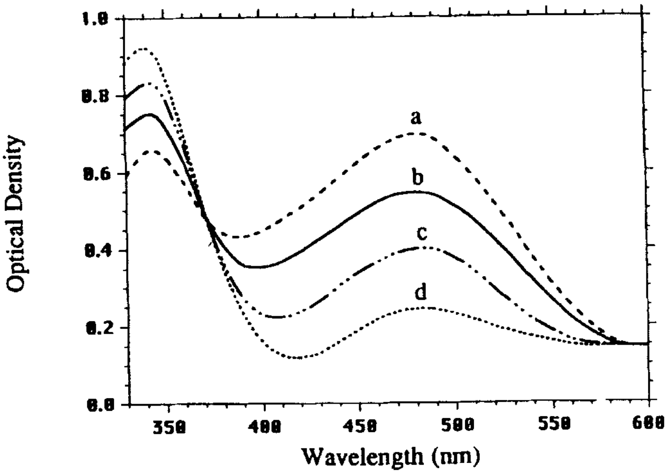


Figure 2 Absorption intensity changes of SP3•HCl with various 450 nm irradiation times. Curves a = unirradiated, b = 10 min irradiation, c = 20 min irradiation, d = 25 min irradiation.

When the base-induced acidichromic SP3 product (SPO$^-$Na$^+$) was irradiated with 365 nm light, the 404 nm-centered absorption band decreased in intensity as a function of irradiation time. At the same time, the 340 nm absorption band intensity increased, again consistent with a secondary photochemical path for regeneration of free SP3 in solution. Thus, SP3 can be reproduced from not only by thermal means but also by photochemical routes.

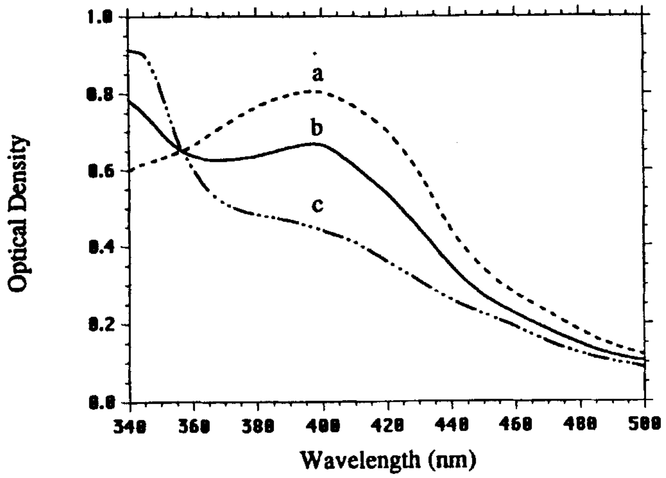


Fig. 3 The absorption spectra change of basic isopropanol solution of SP3 with various irradiation time by 365 nm light.
Curves a = unirradiated; b = 5 min irradiation;
c = 10 min irradiation.

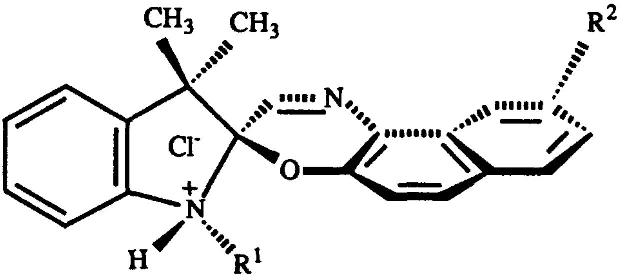
3. Substituent Effects on the Absorption Maxima of Acidichromic Products

The absorption maxima (λ_{max}) of four acidichromic products (SP•HCl) in acidic isopropanol are summarized in Table 1. The difference of absorption maxima of four acidichromic products is due to the 9'-position substituent electron donating effect.

Table 1. λ_{max} of acidichromic product (HCl complex) in isopropanol solutions

Complexes	λ/nm
SP1•HCl	436
SP2•HCl	460
SP3•HCl	490
SP4•HCl	492

The general chemical structure SP•HCl complexes may be represented as indicated in Structure 2.



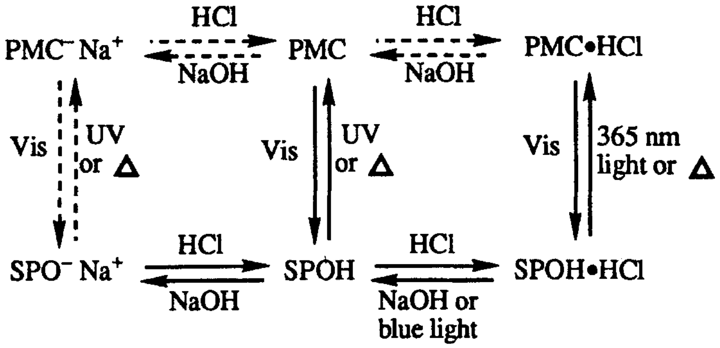
Structure 2

Results reported by Rys *et al.*[8] indicated that protonation of the indolino-nitrogen heteroatom was the dominated structure for spirooxazine-type molecular forms under mildly acidic conditions. These authors, however, did not indicate an absorption peak for spirooxazine in the visible region; instead, the maximum absorption wavelength for the base spiro compound was below 250 nm. It appears from the spectroscopic data gathered on the SP3 and SP4 compounds presently studied that substantial conjugation results from complexation with HCl. This suggests ligation between the protonated indoline nitrogen atom and the Cl^- anion, with donation of p-electron density from Cl^- into the indoline ring. Such donation would serve to yield the more conjugated ring system needed to account for the observed absorption band in the blue region.

4. Comprehensive Discussion of the Acidichromic Mechanism for the Hydroxylated Spirooxazine Compounds

In a previous paper[2], we have mentioned that sodium hydroxide addition to isopropanol solutions of SP1 and SP2 did not yield acidichromic effects. The preparation of SP3 and SP4 compounds, introducing a hydroxyl group at the 9'-position, gives rise to fundamentally different solvent-solute interactions and acid-base chemistry. In the case of SP3 and SP4 solutions, acidichromic effects were observed. The authors have postulated an acidichromic conversion mechanism diagram, given as Scheme I, based on the currently available data. SPOH is a shorthand notation in the scheme indicating the hydroxylated SP3 and SP4 compounds. Reversible conversions which were directly observed are shown as solid arrows, while those which remain conjectured are shown as dashed arrows.

The open photomerocyanine form of SPO^- and SPO^-Na^+ could not be recorded with steady state spectroscopic methods due to the sort-lived nature of these species.



Scheme I. The proposed mechanistic scheme of acidichromism for SP3 and SP4 behavior in isopropanol solutions.

The indicated diagram is supported by the following observations. (1) All of the photon and acid/base induced processes were found to be reversible, a characteristic of acidichromic, photochromic and thermochromic reactions. (2) Hydroxylation of the parent spirooxazine molecule leads to acidichromism effects in both acidic and basic solutions. The SPOH•HCl complex is thermally stable in acidic solutions, while the SPO$^-$Na$^+$ complex was found to be unstable in basic solutions. Decomposition of the SPO$^-$Na$^+$ species is hypothesized to occur by a thermally-initiated mechanism, yielding the parent species through a solvation process. (3) The SPOH•HCl complex was found to exhibit two photochromic pathways. When was irradiated using blue light, (λ_{ex} = 450 nm), it bleached to form SPOH and HCl. The SPOH•HCl complex was slowly reproduced after the irradiating source was turned off. Alternatively, when this complex was irradiated with UV light (λ_{ex}= 365 nm), another photochromic reaction was observed, leading to the indicated photomerocyanine•HCl complex (PMC•HCl). (4) The acidichromic product SPO$^-$Na$^+$ salt, formed under basic conditions, is a newly observed complex, which exhibited unique photochemical behavior and could be induced to reproduce the parent SPOH compound by photochemical means.

While many of the suggested mechanistic processes remain to be substantiated, it is clear these compounds display highly unusual optical properties which may be turned through the use of appropriate chemical conditions.

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REFERENCES

1. X. D. Sun, M. G. Fan, X. J. Meng and E.T. Knobbe J. Photochem. Photobiol. A: Chem 1996 (in press).
2. Y. C. Liang, Y. F. Ming and M. G. Fan, Science in China, B: Chem., (submitted).
3. N. Y. C. Chu, "Spirooxazines" in Photochromism: Molecules and Systems, Edited by H. Durr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990, p493.
4. S. Schneider, F. Baumann, U. Kluter and M. Melzig, Ber. Bunsenges. Phys. Chem., 91 1225 (1987).
5. X. Y. Zhang, S. Jin, Y. F. Ming, Y. C. Liang, L. H. Yu, M. G. Fan, J. Luo, Z. H. Zuo and S. D. Yao, J. Photochem. Photobiol. A: Chem., 80, 221 (1994).
6. C. Bohne, M. G. Fan, Z. J. Li, Y. C. Liang, J. Lusztyk and J. C. Scaiano, J. Photochem. Photobiol. A: Chem., 66, 79 (1992).
7. A. Kellmann, F. Tfibel and R. Guglielmetti, J. Photochem. Photobiol. A: Chem., 91, 131(1995).
8. P. Rys, R. Weber and Q. Wu, Can. J. Chem., 71, 1828 (1993).
9. M. G. Fan, Y. F. Ming, Y. C. Liang, X. Y. Zhang, S. Jin, S. D. Yao and N. Y. Lin, J. Chem. Soc. Perkin Trans. 2, 1387 (1994).