Elucidating the Mechanisms of Acidochromic Spiropyran-Merocyanine Interconversion

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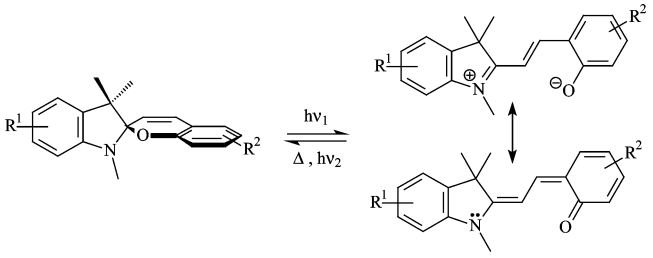
The thermal and photochemical processes associated with the acid-induced conversions of 6-nitroBIPS, **SP-1**, to form the protonated merocyanine (MC−OH^+) were investigated via UV/vis spectrophotometric studies in acetone. It was found that the mechanism of trifluoroacetic acid (TFA)-induced ring-opening of the SP and the rate of MC−OH^+ formation follows a general acid catalysis mechanism. In accord with this mechanism, the thermal growth of the acid-induced ring-opened form (MC−OH^+) was retarded as the concentration of TFA in the medium was increased. The N-protonated SP, i.e., SP−NH^+, is formed in a competing side-equilibrium process as an unreactive "sink", with the nitrogen lone-pair no longer available to drive the ring-opening process and resulting in the inverse rate dependence as a linear $1/k_{obs}$ vs [HA] plot. Addition of a tertiary amine to MC−OH^+ regenerated MC which underwent thermal ring closure to the SP, thus restoring its function as a molecular switch. NMR titration of SP samples showed a downfield shift of the N-substituent peak upon increasing the TFA concentration. However, a saturation behavior could not be observed with **SP-1** up to 1 M acid, unlike the model compound, *N*,*N*-dimethylaniline (*N*,*N*-DMA), which indicates a base strength order of *N*,*N*-DMA > **SP-1**. Further, we have demonstrated that in solvent acetone, on acidification, the normal photo- and thermochromic behavior is reversed; now MC−OH^+ is photochemically transformed into SP−H^+, which undergoes thermal ring-opening to MC−OH^+.

Introduction

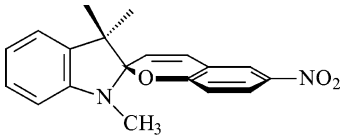
The photochromic behavior of indolino benzospiropyrans (Scheme 1)[1−4] has been under intense investigation for a number of years as part of efforts to exploit its potential in a variety of photonic applications, including high-density optical data storage,[5−8] thin film devices,[9−13] and particle-based technologies.[14−17] Recent work in our laboratory[18−21] and others[22−31] has highlighted applications of spiropyran−merocyanine (SP−MC) transformations as molecular switches. Of particular interest is the characteristic for tuning as a result of structural change as well as through external stimuli.[32−36] While traditionally the commonly employed external stimuli have been thermal and photochemical, modulation of SP−MC systems through acid−base equilibria could have potential advantages as offering additional logic gates[29,37−40] along with interesting consequences upon integration into biological systems.[22,26] A striking example wherein pH control of molecular switching can be monitored by the naked eye has been reported very recently.[41] The reversibility of these molecules may also be effected through electron transfer[42] or metal ion complexation.[43−48]

Numerous authors have examined the mechanisms of the thermal and photochemical transformations in the ring-opening/closure pathways.[49−52] We have delved into examining the effects of medium and substituents on the thermal MC → SP reversion process via solvatokinetic, solvatochromic, and semiempirical studies to gain further insight into the intermediate structures in these pathways so as to circumvent thermal reversion and degradation, deleterious to switching ability of the system.

SCHEME 1



Previously, we reported a novel method for studying the SP−MC equilibrium of nonactivated SPs, consisting of acid-induced ring-opening of the SP followed by neutralization and stopped-flow measurement of ring-closure of the resulting MC.[53,54] These studies have been expanded to include the acid-induced ring-opening of activated SPs (6′-nitro). Accordingly, in this paper, we describe the fundamental mechanisms in the acidochromism of the well-known photochromic SP, 6-nitro BIPS (1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole]), **SP-1**.



SP-1

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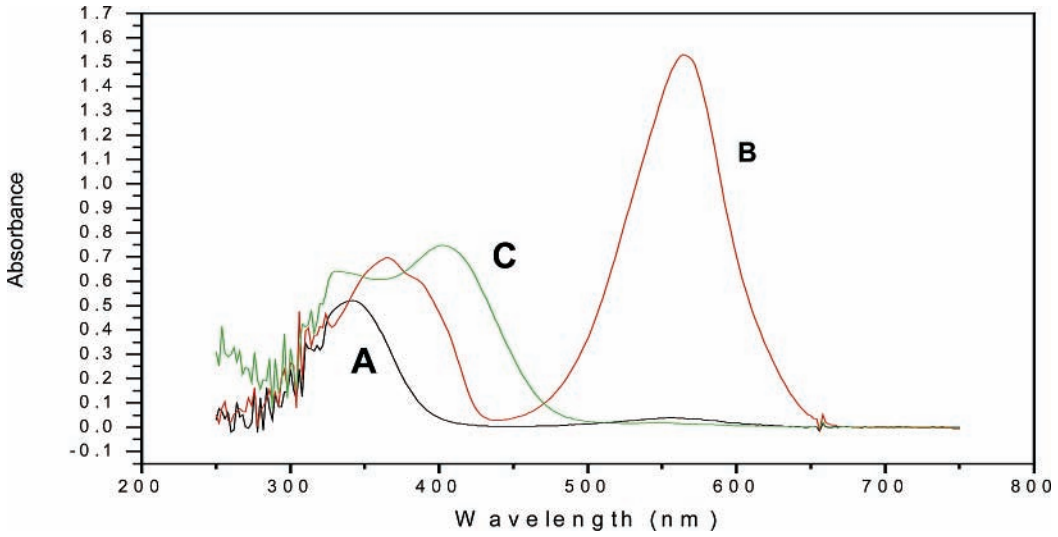


Figure 1. Spectral overlay of the different spectrophotometric species observed in this study: **A**, **SP-1**; **B**, MC-1; **C**, MC−OH$^+$, all in acetone at 25 °C.

Another, less intensively studied, aspect of SP−MC interconversions is the possibility of both normal (positive) and reverse (anti or negative) photochromism, induced thermally or photochemically.[55,56] In the present paper we report on the switching or modulation, from normal to reverse photochromism, through acid−base equilibria.

Experimental Section

General Procedures. All glassware was washed with ethanol and acetone prior to use. All solvents and reagents used in this study were of spectrophotometric grade. *N*,*N*,-Dimethylaniline (Aldrich) was used as supplied. Acetone-d_6 (99.9 atom % D), was purchased from CDN Isotopes and trifluoroacetic acid (TFA) from Aldrich. The photochromic spiropyran 6-nitro BIPS, **SP-1**,was synthesized according to literature procedures.[57]

Spectrophotometric Protocol. Stock solutions of **SP-1** (1×10^{-2} M) and TFA (1 M, 0.1 M) were prepared in acetone. Reproducible results on transformations of the SP to MC in the presence and absence of TFA were obtained by developing a standard protocol for the observation of either photochemical or thermal processes. Briefly, 2.00 mL of acetone was added via syringe into a 1-cm path length quartz cuvette which was sealed with a rubber septum and purged with N_2. The cuvette was placed in a thermostatted (25 °C) cell compartment of an HP 8452A Diode Array Spectrophotometer and a blank spectrum acquired. A 10-μL aliquot of the SP stock solution was injected into the cuvette through the rubber septum via a microsyringe. The SP spectrum was taken to ensure that the concentration of SP in the cuvette was 5×10^{-5} M ($\epsilon \approx 1 \times 10^4$ M^{-1} cm^{-1})

Acidochromic Studies. An aliquot of TFA stock solution was added via microsyringe to the cuvette containing the photochromic SP in acetone, and the cuvette was immediately placed in the spectrophotometer for spectra collection. The spectra were acquired over the range 250 → 750 nm at 5-min intervals for 60 h or until the appearance of MC−OH$^+$ (λ_{MC-OH^+} = 405 nm) was no longer observed. First-order rate constants (k_{obs}) were calculated from plots of the absorbance of MC−OH$^+$ (λ_{MC-OH^+} = 405 nm) vs time and reproducible within 3−5%. Rate data were obtained with concentrations of TFA varying from $1 \times 10^{-4} \rightarrow 7.5 \times 10^{-3}$ M.

Upon stabilization of the MC−OH$^+$ peak at 405 nm in a known [TFA], an equimolar amount of tertiary amine (e.g., tri-*n*-butyl amine) was injected into the cuvette to follow the base-induced ring closure of MC−OH$^+$ → SP. The spectra were acquired over the range 250 → 750 nm at 30 s intervals until the disappearance of MC (λ_{MC} = 558 nm) was no longer observed.

NMR Titration. For the NMR experiments stock solutions of **SP-1** (5×10^{-2} M) and TFA (0.1 M) were prepared in acetone-d_6. Each stock solution was made up in a 5-mL volumetric flask under an inert atmosphere and sealed with a rubber septum and Parafilm, wrapped with aluminum foil, and kept in the dark at 0 °C. Proton NMR spectra were obtained on a Bruker ACF-200 spectrometer, with the chemical shifts reported in δ (ppm) relative to tetramethylsilane. A similar set of NMR titration experiments was performed with *N*,*N*-dimethylaniline (*N*,*N*-DMA). Solutions of *N*,*N*-DMA and **1** were made up in 5-mm inside diameter NMR tubes with acetone-d_6 to yield an analyte concentration within the tube of 0.01 M. Two series of NMR tubes were made up with varying concentrations of TFA (0 → 1 M) and NMR spectra were acquired for each sample immediately after the addition of TFA. For acquisition of the MC−OH$^+$ spectrum, the corresponding **SP-1** solution was left in the dark for 3 days in the presence of the lowest concentration of TFA to ensure that the ring-opening had gone to completion and no **SP-1** remained.

Reverse Photochromism. First, the normal photochromism was initiated by irradiating a solution of **SP-1** in acetone (5×10^{-5} M) for 90 s in a Spectroline UV Cabinet equipped with dual 15 W, 365 nm lamps to yield MC (λ_{max} = 568 nm). This MC solution was immediately acidified via injection of a TFA solution (5×10^{-3} M) and placed in a 4-way temperature controlled cuvette holder that was connected via 400-μm optical fibers to an Ocean Optics spectrophotometer equipped with a 200-W Hg/Xe lamp. By use of this apparatus, the cuvette was irradiated at 408 nm (λ_{max} for MC−OH$^+$), at 25 °C, while simultaneously collecting spectra (250 nm → 750 nm). This solution was irradiated for 10 min at which time the peak at 408 nm was observed to decrease to a steady-state.

Results and Discussion

In previous papers we have explored the SP−MC molecular switch modulated by photochemical as well as thermal stimuli as illustrated in Scheme 1. Herein we report the results of applying one of the most widely available chemical stimuli, i.e.,

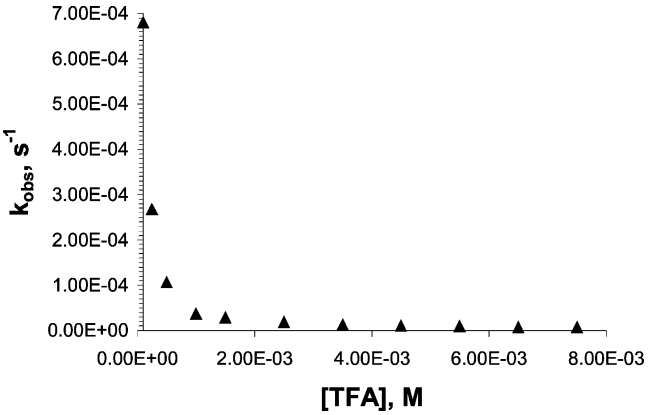


Figure 2. Plot of the observed rate constants for the thermal growth of MC−OH^+ as a function of [TFA], [**SP-1**] = 5.0×10^{-5} M, at 25 °C in acetone.

TABLE 1: Effect of [TFA] on the Observed Rate Constants (k_{obs}) for the Acid-Induced Ring-Opening of SP-1 → MC-1−OH+ at 25 °C in Acetone, [SP-1] = 5×10^{-5} M (Rate Constants Were Reproducible to 3−5%)

	SP-1 + H^+ → MC-1−OH^+
[TFA] M	k_{obs} (10^5 s^{-1})
1×10^{-4}	68.0
2.5×10^{-4}	26.7
5×10^{-4}	10.6
1×10^{-3}	3.63
1.5×10^{-3}	2.83
2.5×10^{-3}	1.82
3.5×10^{-3}	1.23
4.5×10^{-3}	0.768
5.5×10^{-3}	0.892
6.5×10^{-3}	0.677
7.5×10^{-3}	0.673

acidic and basic catalysts, for this purpose. Since the catalytic behavior of these agents is well understood following the classical studies of Bronsted and later, R.P. Bell, and is now enshrined in current texts, their application in the context of molecular switches, appeared to be of promise.

Three Distinct Optical Species: SP, MC, and MC−OH^+. A spectral overlay of the different species observed in this study is given in Figure 1.

In the absence of light and acid, SP solutions in acetone are stable over an extended period of time; the SP−MC equilibrium highly favors the SP form. Injection of an aliquot of trifluoroacetic acid (TFA) to the SP solution causes the absorption at 340 nm to decrease and the appearance over time of another absorption at 402 nm. This peak has been assigned on the basis of UV−vis and NMR evidence as the O-protonated merocyanine, MC−OH^+ form.[57,58]

Acid-Induced Ring-Opening: SP → MC−OH^+. Addition of low concentrations of TFA to **SP-1** in acetone results in a significant decrease in the rate of thermal growth of the MC−OH^+ species ($k_{obs} = 6.8 \times 10^{-4}$ s^{-1}, [TFA] = 1×10^{-4} M). As the concentration of TFA is increased in the solution, the rate decreases by 2 orders of magnitude over the range of TFA used. Rate data in acetone as a function of [TFA] are given in Table 1.

We have found that the rate of formation of the MC−OH^+ species shows inverse dependence on the concentration of TFA. This is demonstrated by the decreasing dependence of k_{obs} on [TFA], Figure 2, and, on the other hand, the linear relationship between $1/k_{obs}$ and [TFA], Figure 3.

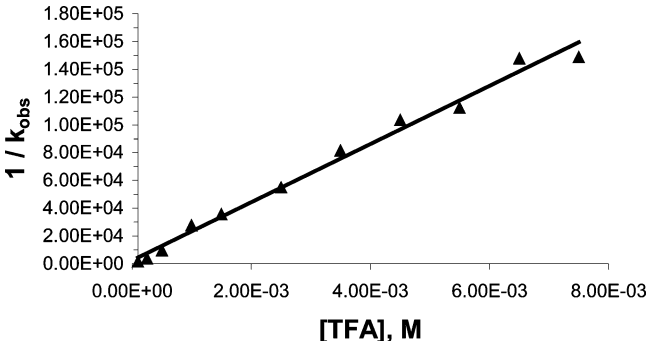
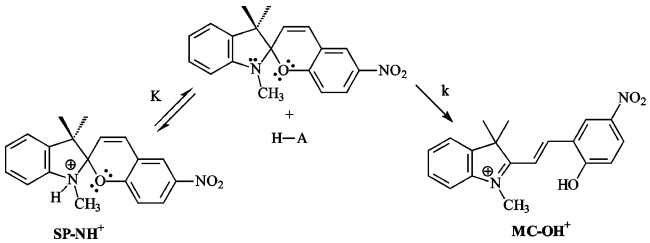


Figure 3. Inverse plot of the observed rate constants ($1/k_{obs}$) for the thermal growth of MC−OH^+ as a function of [TFA], [**SP-1**] = 5.0×10^{-5} M at 25 °C in acetone.

SCHEME 2



The rate dependence demonstrated in Figures 2 and 3 is accommodated by Scheme 2 where HA is an acid, e.g., TFA. Scheme 2 can then be formulated via eq 1

$$\underset{+\ A^-}{SP-NH^+} \overset{K}{\rightleftharpoons} \mathbf{SP} + HA \overset{k}{\rightarrow} \underset{+\ A^-}{\mathbf{MC-OH^+}} \qquad (1)$$

and followed by expressions for the equilibrium constant K where pair represents the ion pair $SP-NH^+A^-$, and c = total concentration of SP, i.e., c = [pair] + [SP]

$$K = [SP]\,[HA]/[pair]$$

Therefore

$$c = [SP] + [SP][HA]/K = [SP]\,(1 + [HA]/K)$$

$$[SP] = c/(1 + [HA]/K)$$

The rate of MC−OH^+ appearance is then given by

$$d[MC]/dt = k[SP] = kc/(1+ [HA]/K) \qquad (2)$$

If it is assumed that [HA] ≫ c, so that it may be considered constant, then the observed rate of the reaction follows as

$$d[MC]/dt = k_{obs}c$$

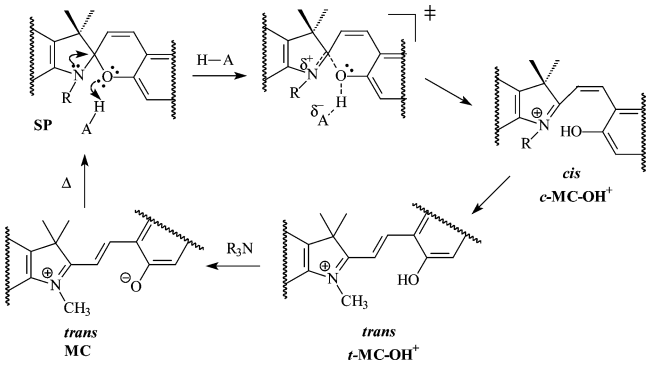
$$\text{and } k_{obs} = k/(1 + [HA]/K) \qquad (3)$$

$$\text{or } 1/k_{obs} = 1/k + [HA]k/K \qquad (4)$$

Then, a linear plot of $1/k_{obs}$ vs [HA] follows with intercept = $1/k$ and slope of k/K as found in Figure 3.

Overall, the reaction scheme depicted in Scheme 2 and eq 1 corresponds to a general acid-catalyzed conversion of SP to the O-protonated ring-opened merocyanine, MC−OH^+, with, however, a competing process, the equilibrium N-protonation of SP, forming $SP-NH^+$. The latter species acts as an unreactive "sink" since the nitrogen no longer has available a lone electron pair to drive the ring-opening process. It is this side equilibrium of

SCHEME 3

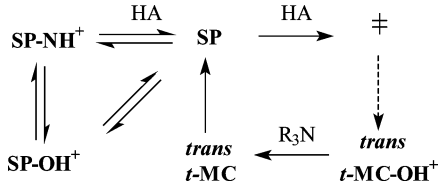


substrate that leads to the inverse rate dependence, $1/k_{obs}$ vs [HA], shown in Figure 3. Spectrophotometric characterization of the SP−NH^+ species could not be obtained in acetone, and attempts to resolve this species from the parent SP were not successful in solvents with greater transparency in the UV region, i.e., acetonitrile, MeOH.

The general acid-catalyzed nature of the reaction leads one to formulate the mechanism in Scheme 3 showing the transition state (TS) and the ring-opening to yield, initially, the *cis*-merocyanine, c-MC−OH^+, followed by its isomerization to the observed *trans*-merocyanine, t-MC−OH^+. The cis−trans isomerization has been discussed previously.[18−20,57,58]

Base-Induced Ring Closure: MC−OH^+ → SP. The role of added base to such a system can now be discussed. Following the TFA-induced ring-opening of the SP (Figure 4A), addition of tri-*n*-butylamine, or other tertiary amine, restored cleanly the

SCHEME 4



spectrum corresponding to the *trans*-merocyanine form, *t*-MC, which then underwent ring closure to the original SP at the rate previously established for the thermal MC to SP process (Figure 4B). The sequential acidochromic ring-opening followed by base-induced ring closure can be represented by Scheme 4.

The oxygen-protonated spiropyran, SP−OH^+, has been included in Scheme 4 as a possible species though the experimental evidence does not support its formation as a reaction intermediate in this system. Had the SP−OH^+ species been formed on the reaction pathway in an equilibrium process, i.e., one subject to specific acid catalysis (A-1), eq 5

$$SP + H^+ \rightleftharpoons SP{-}OH^+ \rightarrow MC \qquad (5)$$

one would have expected to see a linear k_{obs} vs [HA] rate profile showing direct proportionality between k_{obs} and [HA]. In fact, Figures 3 and 4 show an inverse dependence of rate on [HA] thus establishing a general acid-catalyzed mechanism for this acidochromic reaction.

NMR Studies. In order to further quantify the nature of the processes occurring on the molecular level during the acid-induced ring-opening, NMR studies were performed to examine

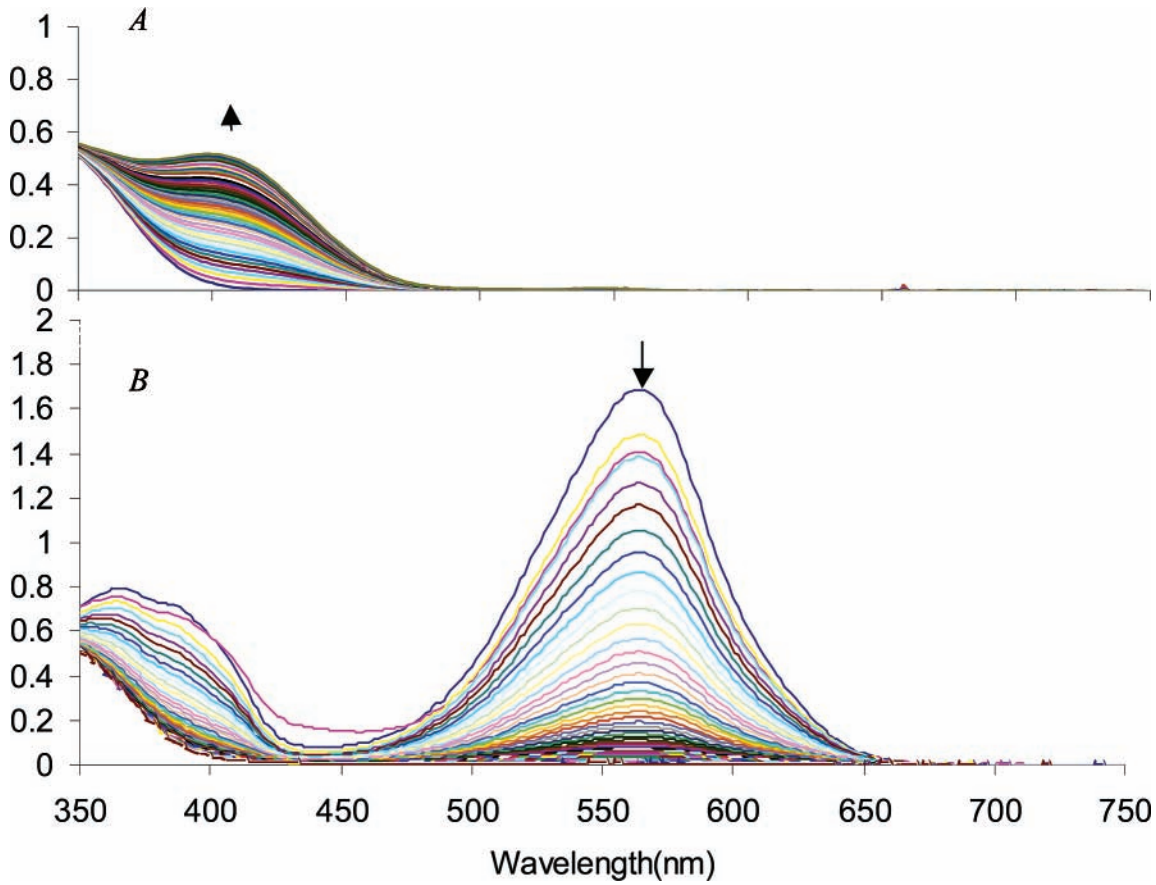
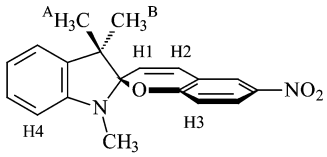
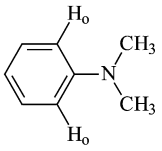


Figure 4. Stacked absorption vs wavelength plots depicting two distinct thermal processes. A, **SP-1** → MC−OH^+ in the presence of [TFA] = 5×10^{-4} M, in acetone at 25 °C, time interval = 600 s; B, thermal reversion of MC → SP after treatment of MC−OH^+ with tributylamine, [TBA] = 5×10^{-4} M, time interval = 30 s.

TABLE 2: Effect of Increasing the [TFA] from 0 → 1 M on Select ^{1}H NMR Signals (δ ppm) of SP-1 and *N*,*N*-DMA in Acetone-d_6, Where [SP-1], [*N*,*N*-DMA] = 0.01 M (All NMR Spectra Were Acquired Immediately upon Injection of TFA Except for MC−OH$^+$ as the Signals in Bold Correspond to the MC−OH$^+$ Form Obtained from SP-1 → MC−OH$^+$ Conversion over 3 d)



SP-1 (**1**)



N,N-DMA (**2**)

	TFA M	0	0.02	0.04	0.08	0.16	0.40	0.80	1.0	MC−OH$^+$
N,*N*-DMA	N−CH$_3$	2.92	3.07	3.14	3.24	3.36	3.51			
	H$_o$	6.75	7.15	7.31	7.49	7.74	7.84			
SP-1	N−CH$_3$	2.77			2.81	2.86	3.07	3.07	3.53	**4.40**
	H1	6.04			6.07	6.14	6.38	6.92	7.03	**7.38**
	H2	7.23			7.26	7.28	7.42	7.75	7.81	**8.71**
	H3	6.88			6.90	6.94	7.12	7.57	7.64	**7.73**
	H4	6.64			6.69	6.75	6.97	7.14	7.16	**8.00**
	CH$_3^A$	1.31			1.28	1.31	1.42	1.70	1.74	**1.95**
	CH$_3^B$	1.20								

the effects of protonation on the chemical shifts of the **SP-1** molecule. To this end, a set of NMR tubes containing **SP-1** and another set containing the model compound, *N*,*N*-DMA in acetone-d_6, were spiked with known amounts of TFA. All these experiments were conducted in the dark, with no irradiation, to ensure that the conditions were analogous to the chemical stimuli observed in the spectrophotometric studies. Chemical shifts monitored were: N−CH$_3$ of each compound; ortho protons (H$_o$) for *N*,*N*-DMA, diastereotopic methyls CH$_3^A$ and CH$_3^B$, vinylic hydrogens H1 and H2, and the ortho hydrogens H3 and H4 for **SP-1** (Table 2). The associated chemical shifts for MC−OH$^+$ were also acquired to compare the extent of **SP-1** protonation to the ring-opened product.

It is apparent that the observed chemical shift changes induced by TFA are indicative of N-protonation. For example, the N-methyl peaks in *N*,*N*-DMA and **SP-1** found at 2.91 and 2.74, respectively, in the absence of TFA, undergo a significant downfield shift with added TFA due to increased positive charge accompanying N-protonation. Interestingly, the two signals CH$_3^A$ and CH$_3^B$ of the diastereotopic methyl groups in **SP-1** coalesced upon addition of TFA but experienced smaller deshielding compared to other relevant proton signals. The coalescence has been attributed previously to acid promoted exchange between the two enantiomers of the SP moiety, in a mechanism involving ring-opening through a *cis*-MC−OH$^+$ intermediate.[57,58] Furthermore, in comparing the chemical shifts of the ring-opened MC−OH$^+$, it is apparent that the downfield shift of the protonated **SP-1** can only be ascribed to N-protonation, i.e., formation of SP−NH$^+$, and not ring-opening as the N−CH$_3$ signal for MC−OH$^+$ is observed much further downfield at 4.40 ppm. Each of the signals that were observed during these experiments demonstrated similar trends and did not exhibit the chemical shifts indicative of the ring-opened *trans*-MC−OH$^+$.

In the case of *N*,*N*-DMA, the results show a marked dependence of chemical shift on [TFA]. The saturation type curve of the N−CH$_3$ singlets in Figure 5 indicates virtually complete protonation over the 0 → 0.4 M acid range studied for *N*,*N*-DMA. In contrast, the plot for **SP-1**, with its weak dependence of chemical shift on TFA is in accord with partial protonation, possibly accompanied by an acid-induced solvent

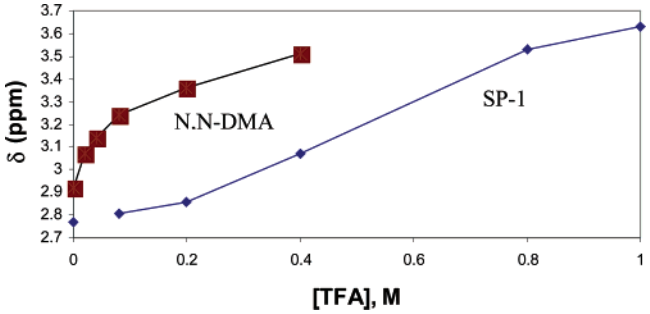


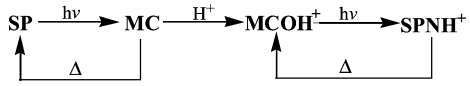
Figure 5. Plots of the N−CH$_3$ chemical shifts of **SP-1**, [**1** (◆)] and *N*,*N*-DMA [**2** (■)] in acetone-d_6 as a function of TFA concentration.

effect on chemical shift. Clearly evident is the weaker basicity of the SP relative to *N*,*N*-DMA. Molecular models for the SP indicate a structure with restricted rotation about N but which allows extensive overlap between the orbital bearing the unshared electron pair on the indolino-N and the benzenoid p-orbital system. This type of "planarization" with lone-pair conjugation would lead to the observed decrease in SP basicity (by analogy with the conventional reasoning ascribing decreased basicity for aniline relative to cyclohexylamine, for example). It is possible also that N-protonation in SP leads to a more sterically hindered ion than does protonation of *N*,*N*-DMA, which would contribute to enhanced basicity of the latter. A theoretical approach could aid in further discussion on this point, such as determination of rotational barriers and preferred conformers.

Overall, the NMR studies described above are fully consistent with the mechanistic schemes that we have proposed for the acidochromic conversion of the spiropyran to the ring-opened merocyanine, with the characteristic inverse dependence of rate on acid concentration displayed in Figures 2 and 3.

Reverse Photochromism. An interesting aspect of acidochromic SP−MC equilibria is the possibility of both normal (positive) and reverse (anti or negative) photochromism, under thermal or photochemical stimuli. This is illustrated schematically below (Scheme 5).

SCHEME 5



In this scheme the initial (left) portion denotes the normal photochemical (UV) ring-opening of SP to yield MC and its reversion thermally or through irradiation with visible light. In juxtaposition is reverse photochromism that occurs from the acidified merocyanine. Now, irradiation of MC−OH$^+$ causes it to ring close to SP−NH$^+$, as evidenced by the decrease in the MC−OH$^+$ absorption at 408 nm over time, from $A_0 = 0.76 \rightarrow A_t = 0.14$ in 10 min. The SP−NH$^+$ once formed underwent spontaneous reversal to MC−OH$^+$, the absorbance at 408 nm increasing from 0.03 to 0.72 in 20 h, thus concluding the cycle with reverse photochromism. Studies of other photochromic systems where switching between normal and reverse photochromism occurs following protonation, are underway.

Conclusion

Investigations into the fundamental mechanisms associated with molecular-based devices are paramount to their eventual application on the nanoscale. In the first part of the current study, the effect of acid concentration on the conversion between three

distinct optical species, SP, MC, and MC−OH^+, has been examined via spectrophotometric and NMR studies. Our study has shown that the acidochromic rate of conversion between SP and MC−OH^+ is inversely proportional to the concentration of acid present in the media; the principles of general acid catalysis can be applied to explain the acidochromic behavior of the SP−MC molecular switch. On the basis of these results, we have developed a mechanism for the ring-opening and ring-closing processes that involves initial protonation of the basic indolenine moiety which explains how protonation reduces the rate of molecular switchability (usually an undesireable effect). It is an important implication of this mechanism that the local concentration of acid and base will have to be strictly controlled for this system to operate efficiently upon exposure to multiple external stimuli that are capable of inducing the switch.

Further, through delineating both normal and reverse acidochromic processes, we have shown that the SP−MC molecular switch which traditional investigations have considered simply as SP ⇔ MC interconversion, e.g., through substituent and solvent dependence, can be extended in acidic media to a system of four different chemical and optical species, SP, MC, SP−NH^+, and MC−OH^+. In these environments, thermal and photochemical stimuli can be employed to switch between each species, with MC−OH^+ being the most thermodynamically stable. This work opens the possibility of manipulating the switchability of these systems through protonation, via thermal and photochemical stimuli, in other photochromic systems and sheds further light on the integration of these systems into applications that rely upon the transduction of multiple stimuli at the molecular level.

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