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Detailed investigation on a negative photochromic spiropyran

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Abstract

The negative photochromic properties of a spiropyran are investigated in various solvents and in solutions of different acidity. The results indicate that the polarity of the solvent has a prominent effect on λ_{max} of the coloured merocyanine form (MC), whereas its effects on λ_{max} of the closed form (SP) and on the coloration rates after visible bleaching are very weak. From the effect of acid concentration on the coloration rates the pK_a of the cis intermediate Y in the coloration process is determined to be about 1.1 lower than that of the protonated merocyanine (MCH^+). The structures and configurations of MC, SP, MCH^+ and Y are assigned via their ^1H NMR spectra.

Keywords: Spiropyran; Negative photochromism; Solvatochromism; pH effect; ^1H NMR

1. Introduction

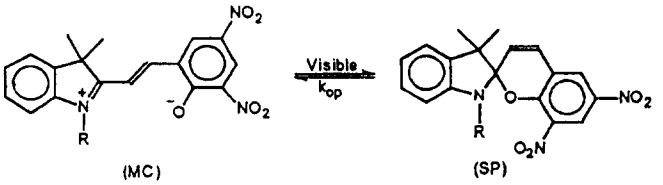
Photochromism is the reversible change in a single chemical species between two states with distinguishably different absorption spectra [1,2], such a change being induced in one direction by the action of electromagnetic radiation, while the change in the other direction is thermally induced and usually occurs spontaneously. When the thermodynamically less stable state is the more deeply coloured form, the system is called a "positive" photochromic system, otherwise it is called a "negative (or inverse)" photochromic system. Most spiropyrans (SPs) and related compounds show positive photochromism. They can be photochemically transformed by UV irradiation into an intensely coloured merocyanine and then decolorated to the colourless form by ring closure in the dark or under visible irradiation. The photochemical opening of the spiro bond or the thermal ring closure will necessarily involve the passing of the system through a cisoid conformation denoted as X [3,4]. Because the coloured form and X are unstable, their identification is always carried out at low temperature [5] or by time resolution spectroscopic methods [6–8].

A few spiropyrans, especially those with free hydroxy, carboxy or amine groups, exhibit so-called "negative" photochromism [9–12]. Recently it was found that replacing the benzopyran moiety by a dihydroquinoline unit with its spiro-C-bonded nitrogen atom further incorporated into another annealed imidazole [4] or replacing the disubstituted phenyl ring of the benzopyran moiety by a benzothiapyrylium [13] makes the molecule "negative" photochromic. For such systems it is convenient to determine the conformation of the stable species in the coloured form in order to get some information about the intermediate X.

In this work the "negative" photochromic properties of a spiropyran in various solvents are studied via UV–visible and ^1H NMR spectra. The effects of pH on the coloured and colourless forms are investigated in detail.

2. Experimental details

The negative photochromic compound 1′-octadecyl-3′,3′-dimethyl-6,8-dinitro-spiro[2*H*-1-benzopyran-2,2′-indoline] (**I**; Scheme 1) is synthesized according to the conventional method (m.p. 141–142 °C) [14]; its structure is confirmed by elemental analysis and spectroscopy.



Scheme 1. Compound I.

SSDI 1010-6030(95)04082-X

All solvents are analytical reagents and are retreated before use. For the adjustment of acidity, 1 mol l^{-1} HCl in acetonitrile is used.

Absorption spectra are recorded on an HP8452 diode array spectrophotometer. The rate constants for the thermal coloration of SP in various solvents are obtained by fitting the experimental data to the equation [15,16]

$$\ln(A_\infty - A_t) = -kt + \ln(A_\infty - A_0) \quad (1)$$

where A_0, A_t and A_∞ are the absorbance of the coloured merocyanine or its protonated form at times 0, t and ∞ respectively. The pK_a value of the open merocyanine form is determined from the equation [16]

$$pK_a = pH - \log\left(\frac{A - A_{MCH}}{A_{MC} - A}\right) \quad (2)$$

where A is the absorbance measured at the long wavelength band maximum for the merocyanine form and A_{MCH} and A_{MC} denote the absorbances measured at the same wavelength when only the protonated (MCH^+) and free (MC) forms of merocyanine are present respectively. A 500 W xenon lamp combined with an interference filter is used for continuous irradiation. The cell is equipped with a magnetic stirrer. ^1H NMR spectra are recorded on a Varian UNITY200 instrument.

3. Results and discussion

3.1. Coloration kinetics in various solvents

In the organic solvents used, the coloured form of **I** is the more stable form. One reason for this is the stabilization of the phenolate anion of the coloured form by the introduction of the second electron-withdrawing nitro group at the 8 position. Fig. 1 shows the visible spectra of the coloured form of **I** in various solvents. It can be seen that, similarly to the photomerocyanines of positive photochromic spiropyrans,

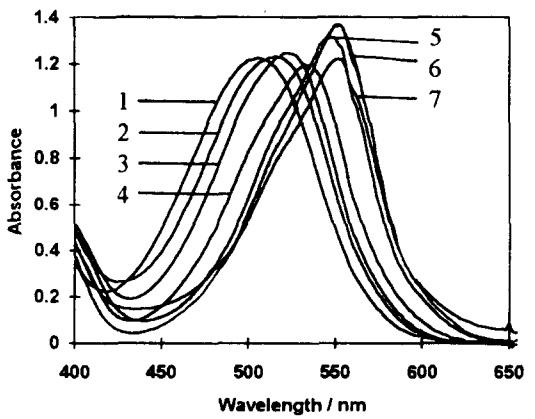


Fig. 1. Visible spectra of the coloured form of **I** in various solvents: 1, methanol; 2, ethanol; 3, acetonitrile; 4, acetone; 5, 1,2-dichloroethane; 6, chloroform ($CHCl_3$); 7, tetrahydrofuran (THF).

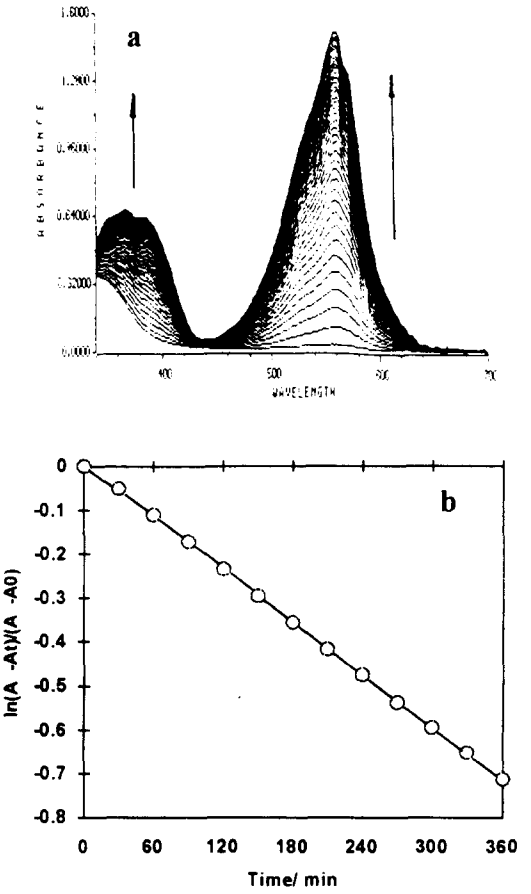


Fig. 2. (a) Coloured form formation and (b) rate constant plot for first-order coloration of **I** in $CHCl_3$ after visible irradiation at 26 °C; time interval 30 min.

there is a blue shift in the absorption band as the polarity of the solvent is increased.

By comparing the electronic transition energies of **I** with Dimroth et al. and Reichardt's $E_T(30)$ [17,18] and Kosower's Z [19] values, we have

$$E_T = 0.277E_T(30) + 40.78, \quad r = 0.966 \quad (3)$$

$$E_T = 0.193Z + 39.72, \quad r = 0.963 \quad (4)$$

This indicates that the absorption processes of the coloured form of **I**, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-phenoxide ($E_T(30)$) and 1-ethyl-4-methoxycarbonylpyridinium iodide are similar solvent-dependent processes.

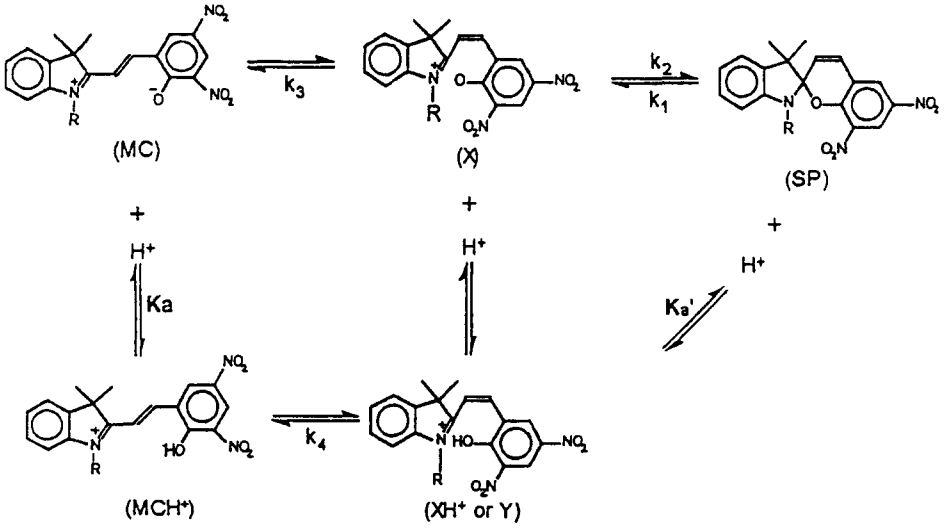
Fig. 2 shows the UV–visible spectral changes of **I** in $CHCl_3$ after visible light bleaching of the coloured form vs. time. The coloration process can be described by Eq. (1) very well. For the coloration process in other solvents, similar results can be obtained. The λ_{max} values of the merocyanine and closed forms of **I** and the first-order rate constants in various solvents are listed in Table 1.

For positive photochromic merocyanines the polarity of the solvents has a prominent effect on the decoloration rate of the photoinduced merocyanine and there is a linear relation between the logarithm of the decoloration rate constant and the transition energy (E_T) [20,21]. From the linear relation

Table 1
Values of λ_{max} and coloration rate constants of I in various solvents at 26 °C

Solvent	Methanol	Ethanol	Acetonitrile	Acetone	1,2-Dichloroethane	THF	$CHCl_3$
λ_{max} (nm), MC	512	522	528	540	554	558	558
λ_{max} (nm), SP	336	344	344	338	338	332	338
$k_{ob} \times 10^5$ (s^{-1})	4.20	3.58	5.44 [a]	3.72	3.66	6.69 [b]	3.30
$t_{1/2} \times 10^{-4}$ (s)	1.65	1.93	1.28	1.86	1.89	1.03	2.10

[a] At 27.5 °C.
[b] At 29 °C.



Scheme 2. Photochemical and physicochemical equilibria for I in solution.

between the logarithm of the decoloration rate constant, the equilibrium constants of the coloured and colourless forms and the transition energy of the coloured form we have found that the polarity of the solvent has a relatively minor effect on the ring-opening rate [22]. In the present work the ring-opening rate constants in various solvents can be easily measured. From Table 1 it can be seen that the polarity of the solvent has little effect on the rate constant of the thermal ring-opening process of the closed form. This again supports our viewpoint in previous work [22] that, unlike the coloured merocyanine, the closed form and the intermediate X in the coloured form formation process are species with less polarity (see Scheme 2).

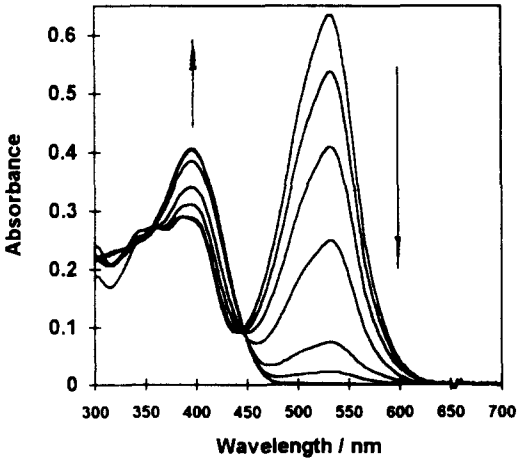


Fig. 3. UV–visible spectra of 1.65×10^{-5} mol l^{-1} I in coloured form in acetonitrile at various concentrations of HCl: 0, 3.2×10^{-5}, 6.4×10^{-5}, 1.6×10^{-4}, 4.0×10^{-4}, 8.0×10^{-4}, 2.0×10^{-3} mol l^{-1}.

3.2. pH effect

The colourless and coloured forms of a spiropyran are distinct chemical species and may undergo different chemical reactions. One highly reactive functional group present in the coloured form only is the phenolate anion. Thus in the presence of acid the coloured form of I may steadily transform into the protonated form MCH^+. Fig. 3 shows the absorption spectra of MC at various concentrations of HCl. From this we have $pK_a = 3.93$. Like the positive photochromic spiropyran, the protonated form of MC is also photochromic. Fig. 4 shows the spectral changes of I at various concentrations of HCl after irradiation at 400 or 528 nm. By fitting the data

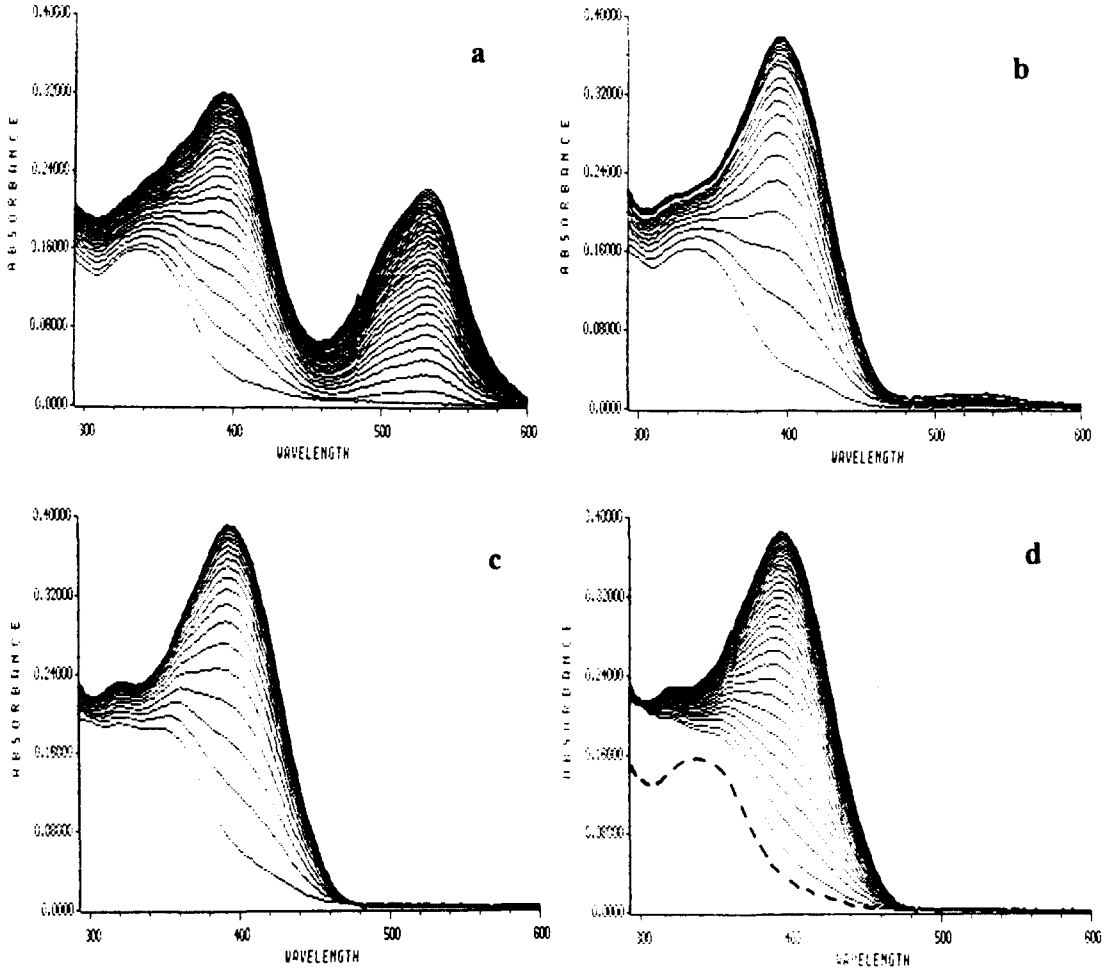


Fig. 4. Formation processes of MC or its protonated form (MCH^+) at various concentrations of HCl after irradiation at 528 or 400 nm: (a) $[HCl] = 2.0 \times 10^{-4}$ mol l^{-1}, time interval 20 min; (b) $[HCl] = 8.0 \times 10^{-4}$ mol l^{-1}, time interval 4 min; (c) $[HCl] = 1.76 \times 10^{-3}$ mol l^{-1}, time interval 2 min; (d) $[HCl] = 6.4 \times 10^{-3}$ mol l^{-1}, time interval 1 min; broken curve, spectrum of colourless form from (a).

Table 2
Formation rate constants of MCH^+ at various concentrations of HCl

[HCl] (mol l^{-1})	4.6×10^{-4}	8.0×10^{-4}	1.8×10^{-3}	3.2×10^{-3}	6.4×10^{-3}	1.0×10^{-2}	5.0×10^{-2}
k_{ob} (s^{-1})	4.68×10^{-4}	8.18×10^{-4}	1.52×10^{-3}	1.65×10^{-3}	1.76×10^{-3}	1.88×10^{-3}	2.14×10^{-3}

from Fig. 4 to Eq. (1), k_{ob} values at various concentrations of HCl can be obtained. They are listed in Table 2.

Bercovici et al. [23] reported that when the protonated open form of spiropyran was irradiated with visible light or the closed form of it was treated with a large excess of acid at low temperature, an intermediate Y could be observed in alcoholic solutions but not in methylcyclohexane. This intermediate was attributed to some form of protonated species and can be transformed to the protonated open form at elevated temperature. In more recent work by Drummond and Furlong [16] a similar intermediate was assigned as the cis isomer of the protonated open form, but the direct evidence for this is insufficient. From Fig. 3 it can be seen that when the HCl concentration is low (less than about 8.0×10^{-4} mol l^{-1}), the MC form will coexist with the protonated MCH^+ form. In this situation there exist more than two species in the solution during coloration after visible light bleaching of MC and MCH^+ and no isosbestic point can be observed in the UV–visible spectra (Fig. 4a). At higher concentrations of HCl (greater than about 1.0×10^{-3} mol l^{-1}) the protonated merocyanine MCH^+ is the only species in the coloured form (Fig. 3). Also, if the ring-closing spiropyran is the only species in the colourless form, there should be an isosbestic point on the spectra during coloration after light bleaching of MCH^+. However, such an isosbestic point (304 nm) can only be observed at HCl concentrations higher than 6.4×10^{-3} mol l^{-1} (Fig. 4d). This implies that there exists more than one species in the colourless form at HCl concentrations lower than 6.4×10^{-3} mol l^{-1}. When the concentration of HCl is lower than 8.0×10^{-4} mol l^{-1}, the ring-closing

spiropyran exists in the colourless form. When the concentration of HCl is higher than 6.4×10^{-3} mol l^{-1}, it transforms into the protonated cis open form (Y) and the formation process of MCH^+ should be a uniform reaction. When the concentration of HCl lies between 8.0×10^{-4} and 6.4×10^{-3} mol l^{-1}, SP and Y will coexist after visible light bleaching (Figs. 4b and 4c) and the formation of MCH^+ should not be a uniform reaction. From the absorbance diagram (or *E* diagram) [24] we find that there are no good linear relations between the absorbance at various wavelengths in the MCH^+ formation process when the HCl concentration is low (e.g. Figs. 4a–4c). This indicates that the process is not a uniform reaction. When the HCl concentration is higher (greater than about 6.4×10^{-3} mol l^{-1}, Fig. 4d), the *E* diagram yields straight lines for the combinations of absorbances at various wavelengths, showing that the formation process of MCH^+ is a uniform reaction. By comparing the spectra of the light-bleached solutions at various concentrations of HCl (Fig. 4d), it can be seen that accompanying the formation of Y, λ_{max} shifts towards the long wavelength region and the intensity increases, as Bercovici et al. [23] reported.

From Table 2 it can be seen that the formation rate constant of MCH^+ increases as the concentration of HCl is increased. To understand the effect of protonation further, the formation process of MCH^+ is determined with a solution bleached before acidification; the results indicate that the sequence of adding the acid has no prominent effect on the formation rate of MCH^+. This implies that the transformation of Y to MCH^+ is the rate-limiting step in the formation process of MCH^+ and that the protonation of SP is a fast process (Scheme 2). If the solution of SP is treated with acid (1×10^{-2} mol l^{-1}) for a few minutes before adding the buffer solution, the coloured MC can be formed steadily. If the buffer solution is added immediately after adding the acid, the amount of MC will be greatly diminished.

Because the protonation of SP to Y is a fast process, the formation of MCH^+ at various concentrations of acid can be treated in the following way:

$$\frac{d[MCH^+]}{dt} = -\frac{d[Y]}{dt} - \frac{d[SP]}{dt}$$

$$= k_{ob}([Y]+[SP]) = k_4[Y] \quad (5)$$

or

$$k_{ob} = \frac{[Y]}{[H^+]+[SP]}k_4 \quad (6)$$

Introducing the equilibrium constant

$$K'_a = \frac{[H^+][SP]}{[Y]} \quad (7)$$

into Eq. (6), we have

$$k_{ob} = \frac{[H^+]}{[H^+]+K'_a}k_4 \quad (8)$$

or

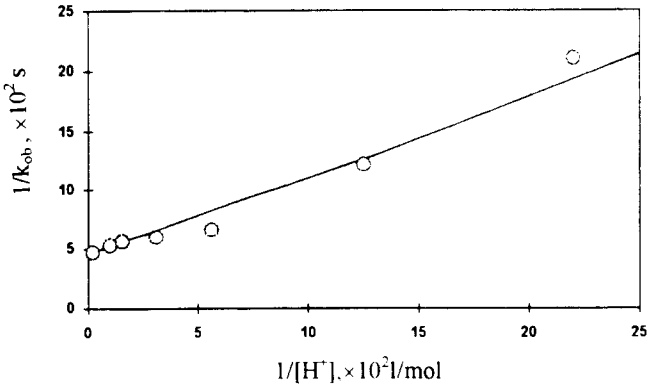


Fig. 5. Plot of $1/k_{ob}$ against $1/[H^+]$.

$$\frac{1}{k_{ob}} = \frac{1}{k_4} + \frac{K'_a}{k_4[H^+]} \quad (9)$$

From the data in Table 2 and Eq. (9), Fig. 5 can be obtained. Then we have $k_4 = 2.17\times10^{-3}$ s^{-1} and $K'_a = 1.51\times10^{-3}$ ($pK'_a = 2.82$). This implies that Y is more acidic than MCH^+.

At 23 °C the formation rate constant of MC in neutral acetonitrile is about 1.8×10^{-5} s^{-1}. In terms of the involvement of the open form X, this rate constant may be expressed as [4]

$$k_{(SP\rightarrow MC)} = k_3\frac{k_1}{k_2} \quad (10)$$

The equilibrium constant between SP and X may be estimated as

$$K_{(SP\rightarrow X)} = \frac{k_1}{k_2} = \frac{k_{(SP\rightarrow MC)}}{k_3} \quad (11)$$

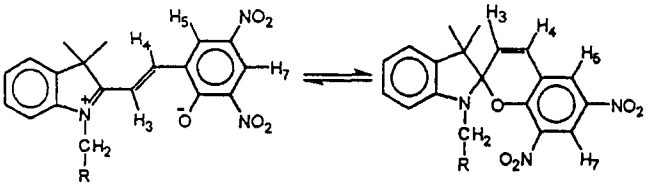
Since the rate constants of the cis–trans isomerization reactions of X to MC and of Y to MCH^+ are nearly the same [4], i.e. $k_3 = k_4$, then we have

$$K_{(SP\rightarrow X)} = \frac{k_{(SP\rightarrow MC)}}{k_4} = 8.3\times10^{-3} \quad (12)$$

3.3. ^1H NMR spectra

Like the indoline spiropyran studied in this work, some derivatives of benzothiazoline spiropyrans are also photochromic. They can form very stable photomerocyanines and their ^1H NMR spectra have been recorded already in DMSO-d_6 [25]. A significant characteristic of the ^1H NMR spectra of the photomerocyanines is that, unlike that of the closed form, the chemical shift of the *N*-methyl group is comparable with that of the heterocycloammonium salts. For the photochromic spiro-oxazines, which are compounds closely related to spiropyrans, such a result cannot be observed [26–28]. In recent work by Keum et al. [29] the ^1H NMR spectra of the closed form of some indoline spiropyrans were reported. To our knowledge, no detailed ^1H NMR spectra of the coloured

Table 3
^{1}H NMR chemical shifts (in ppm) and coupling constants (in Hz) of the spiropyran **I** or its coloured form in acetone-d_6 under various conditions



Proton	H_3	H_4	H_5	H_7	N–CH_2	$J(H_3,H_4)$	$J(H_5,H_7)$
Coloured form	8.56	8.95	8.59	9.65	4.60	15.5	3.0
SP form	6.27	7.38	8.44	8.60	3.29	10.5	2.5
(SP-1) [a]	(6.24)	(7.38)	(8.43)	(8.57)		(10.5)	(2.5)
Coloured form + D_2SO_4	8.25	8.70	9.08	9.12	4.85	16.6	2.5
SP + D_2SO_4 at −50 °C	7.37	7.71	8.62	9.02	4.30	13.5	2.6

[a] From Ref. [27] for **I** with a methyl group at the N atom of indoline.

forms of indoline spiropyrans or their various protonated forms have been reported.

For the determination of the structures and configurations of the various species formed from **I** under different conditions, the ^{1}H NMR spectra of **I** are recorded. Because the solubility of **I** in acetonitrile is too low, the NMR spectra are obtained in acetone. Fig. 6 shows the NMR spectra of **I** in acetone before and after visible irradiation. Data from Fig. 6 and other conditions valuable for the assignment of the corresponding structures and configurations are collected in Table 3.

From Fig. 6 and Table 3 it is obvious that unlike the ring-closing form (SP) of **I** and the coloured forms of some spiro-oxazines, the chemical shift of the N–CH_2 group in the coloured form (4.60) is comparable with that of 1-octadecyl-2,3,3,-trimethyl indolinium iodide (4.68). This indicates that the open form (MC) of **I** is a more polar species than SP ($\delta_{N-CH_2}=3.29$) or the open form of spiro-oxazine ($\delta_{N-CH_3}=3.70$). Also it is reasonable to represent it by a zwitterionic structure (Scheme 1). The olefinic protons (H_3 and H_4) with a coupling constant $(AB)^3J=15.5$ Hz appear at 8.56 and 8.90 respectively. This clearly indicates that the trans conformation is the stable isomer of MC [30]. When MC is deuterated by D_2SO_4, the signal of N–CH_2 shifts to lower fields, implying that the positive charge density at the N atom is increased. From the coupling constant of the olefinic protons (16.5 Hz) the conclusion that MCH^+ has a trans conformation similar to that of MC may be drawn. At low temperature, when SP is treated with D_2SO_4, the spectrum is quite different from those of SP, MC and MCD^+; it is reasonable to attribute it to Y. Comparing the chemical shift of its N–CH_2 group with those of SP, MC and MCH^+, it can be found that the signal appears at lower fields than for SP but at higher fields than for MCD^+ or unprotonated MC. This means that the two parts of Y do not conjugated each other as well as in MCH^+ or MC. The olefinic protons (H_3 and H_4) of Y, appearing at 7.37 and 7.71 respectively, have a coupling constant of 13.5 Hz, which is larger than for the cis form SP but less than for the trans form MC. Thus the conformation of it should not be a coplanar cis form.

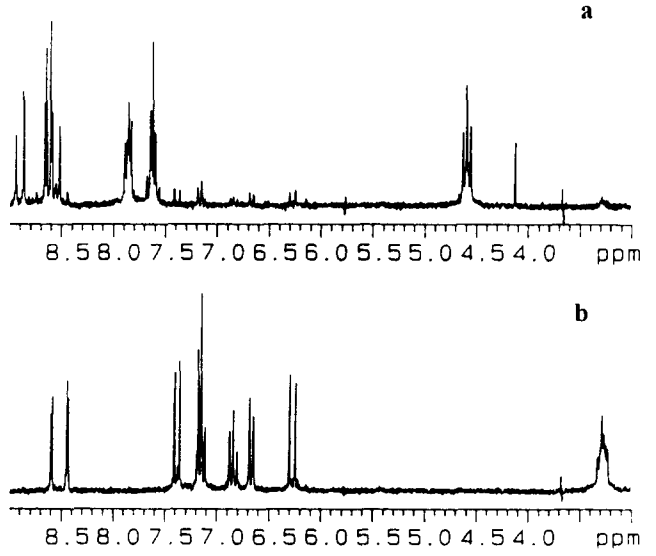


Fig. 6. ^{1}H NMR spectra of **I** in acetone (a) before and (b) after irradiation with visible light.

4. Conclusions

The following conclusions can be drawn.

(1) Unlike the decoloration processes of the positive photochromic spiropyrans, the change in the polarity of the solvent has less effect on the coloured form formation rate of the present negative spiropyran after visible light bleaching of the coloured form.

(2) In the presence of acid there exists a fast equilibrium between SP and its protonated intermediate Y, which then transforms to the protonated merocyanine (MCH^+). From the effect of acidity on the rate of MCH^+ formation the pK'_a of Y is estimated to be 2.82. This indicates that the acidity of Y is stronger than that of MCH^+.

(3) From ^{1}H NMR spectra we found that MC and MCH^+ are favoured in the trans conformation, while Y occurs in a unique twisted cis conformation.

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