

# Correlations between solvatochromism, Lewis acid–base equilibrium and photochromism of an indoline spiropyran

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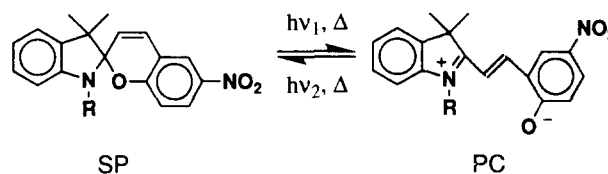
## Abstract

The solvatochromism, Lewis acid–base equilibrium and photochromism of an indoline spiropyran in neat and mixed organic solvents were studied by UV–visible spectroscopy. The variation of the transition energy  $E_T$  of the coloured form (PC) in different solvents was used as an empirical parameter to measure the polarity of the solvents and as a reference process to predict the shift of the Lewis acid–base equilibrium between PC and the colourless form (SP) and the thermal decolouration rates of the PC form in neat and mixed organic solvents. From the linearity of the plot of  $\ln K_e$  or  $\ln k_{dc}$  vs.  $E_T$ , the Lewis acid–base equilibrium, photochromism and solvatochromism of the spiropyran were found to be similar solvent-dependent processes. The changes in  $K_e$  and  $k_{dc}$  were interpreted in terms of the differences in solvation of PC in solvents of different polarity. The relatively small influence of solvent polarity on the colouration rate  $k_{op}$  serves as evidence supporting the view that the rate-determining ring-opening process is a concerted electrocyclic reaction.

**Keywords:** Solvatochromism; Lewis acid/base equilibrium; Photochromism; Spiropyran

## 1. Introduction

The thermochromism and photochromism of spiropyrans have been noted for many years [1]. Spiropyrans and related compounds (e.g. spirooxazines) continue to attract strong interest in connection with their applications in various fields, such as non-silver high-resolution photography, optical devices and variable transmission materials [2]. With the formation of the photomerocyanine form, which accompanies heterolytic cleavage of the C–O bond (Scheme 1, the absorption band shifts from the UV to the visible region. Like other merocyanines, the photomerocyanine or spiropyran open form (PC) is a negative solvatochromic dye, i.e. with increasing solvent polarity, the absorption band undergoes a hypsochromic (or blue) shift. In order to describe the effect of the solvent on the electronic spectra, the absorption maxima of PC (expressed in wavenumbers) or the transition energies are plotted against solvent polarity parameters, such as  $E_T(30)$  values [3], Kosower's  $Z$  values [4], Brooker's  $X_B$  values [5] and Brownstein's  $S$  values [6], and reasonably linear plots are obtained. In addition to the solvatochromic effect, the solvent may also affect the intramolecular Lewis acid–base equilibrium between SP and the stereoisomers of PC and the decolouration rates of PC. We have found that



Scheme 1. Thermochromism and photochromism of indoline spiropyran.

the changes in the absorption maxima, acid–base equilibrium and decolouration rate of the PC form of this compound are intrinsically solvent dependent. Therefore this compound may serve as a model system for studying the correlation between spectra and reactivity.

## 2. Experimental details

1'-Hexadecyl-3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (SP-16) was synthesized according to the procedure reported by Gruda and Leblanc [7]. Its melting point was 87–88 °C (84–85 °C [7], 86–87 °C [8]). The proton nuclear magnetic resonance ( $^1\text{H NMR}$ ) spectrum was as expected.

All solvents were analytically pure and were re-treated before use. A Hewlett-Packard HP8452A diode array UV–visible spectrophotometer was used to record the spectra. The

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Table 1  
Values of  $\lambda_{\max}$  and  $A_e$  of the PC form of SP-16 and  $K_e$  in neat organic solvents at 31 °C

Solvent	$\lambda_{\max}$ (nm)	$C \times 10^3$ (mol l <sup>-1</sup> )	$A_e$	$K_e \times 10^3$
Methanol	533	1.0	2.14	62.0
Ethanol	543	2.0	1.65	22.0
Isopropanol	551	2.0	0.746	10.6
Acetonitrile	560	1.0	0.280	9.30
Acetone	571	2.0	0.270	3.05
1,2-Dichloroethane	580	2.1	0.184	2.50
Butanone	574	4.9	0.379	2.21
Tri- <i>n</i> -butylphosphate	582	5.2	0.254	1.39

solutions were irradiated by a 500 W high pressure mercury lamp with a suitable filter.

To determine the equilibrium constants  $K_e$  between SP and PC in various solvents, solutions of SP-16 were prepared at concentrations giving measurable intensities of absorption in the visible region. They were kept at room temperature in the dark for 12 h. To determine the concentration of the visible-light-absorbing PC form,  $\epsilon = 3.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  for the PC form of SP-1 in ethanol was used in polar solvents according to Flannery [9], who reported that the influences of  $\epsilon$  on the derived thermodynamic data are relatively small. At equilibrium, from Beer's law, we have

$$K_e = \frac{[\text{PC}]}{[\text{SP}]} = \frac{A}{3.5 \times 10^4 \times C - A} \quad (1)$$

where  $K_e$  is the equilibrium constant between PC and SP,  $A$  is the equilibrium absorbance at the absorption maximum and  $C$  is the total concentration of spiroopyran initially dissolved. The decolouration rate constant of the photoinduced PC form of SP-16 in solution is obtained by Eq. (2) as shown by Drummond and Furlong [3]

$$\ln(A_t - A_e) = -k_{\text{dc}}t + \ln(A_0 - A_e) \quad (2)$$

where  $A_0$ ,  $A_t$  and  $A_e$  are the absorbances of the PC form at time 0,  $t$  and at equilibrium respectively and  $k_{\text{dc}}$  is the decolouration rate constant of PC.

### 3. Results and discussion

#### 3.1. Solvatochromism

In apolar solvents, such as benzene, cyclohexane, etc., the existence of more than one kind of interconvertible species of the SP-16 PC form makes the analysis of the equilibrium and decolouration processes more complicated. In this work, eight polar solvents were used in the absorption measurements. Table 1 shows the absorption maxima and absorbance of the PC form in equilibrium with the SP form ( $A_e$ ) in neat organic solvents at different concentrations. It can be seen that the  $\lambda_{\max}$  values of the PC form undergo a bathochromic shift as the polarity of the solvent decreases. By plotting the transition energies  $E_T$  of the PC form of SP-16 vs. the  $E_T(30)$  values of the solvents [10], good linearity can be obtained

$$E_T(\text{SP-16}) = 0.306E_T(30) + 37.0 \quad (n=8, r=0.990) \quad (3)$$

The excellent correlation between the  $\pi-\pi^*$  transition energies of the PC form and  $E_T(30)$  implies that the contributions of different solute-solvent interaction forces, as measured by the solvatochromic pyridinium-*N*-phenoxide betaine dye, are nearly the same as for the  $\pi-\pi^*$  absorptions of PC of SP-16. The transition energy of the PC form can be used as a measure of the micropolarity of the solvent on the molecular level. Fig. 1(a) shows the spectra of  $2.0 \times 10^{-3} \text{ mol l}^{-1}$  SP-16 in ethanol-acetone mixtures. As the amount of acetone increases, a bathochromic shift of the absorption band of PC is observed (Fig. 1, Table 2). The  $\lambda_{\max}$  values are not a linear function of the solvent composition. This may be caused by the preferential or selective solvation of PC by the more polar solvent ethanol in this binary solvent system.

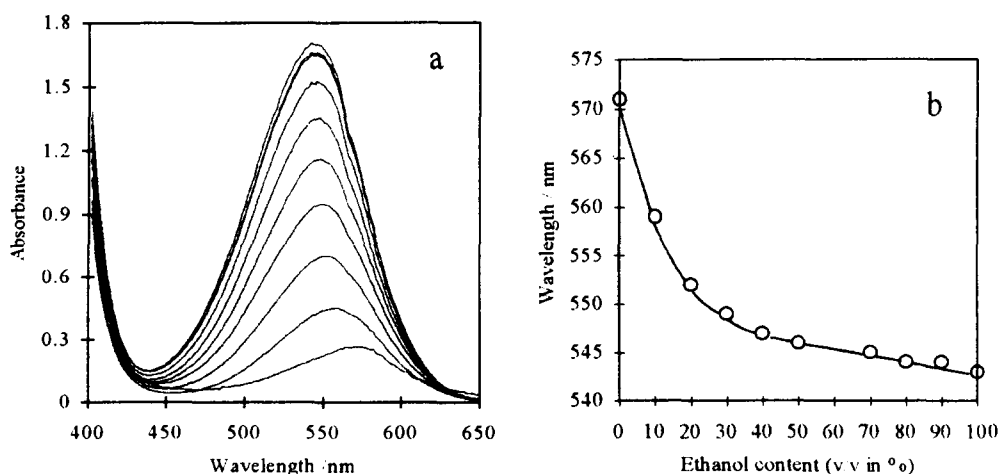


Fig. 1. (a) Variation of the visible spectrum of  $2.0 \times 10^{-3} \text{ mol l}^{-1}$  SP-16 in ethanol-acetone mixtures. Ethanol content (v/v (%)): 0, 10, 20, 30, 40, 50, 70, 80, 90, 100. (b)  $\lambda_{\max}$  of the coloured form of SP-16 as a function of the amount of ethanol in ethanol-acetone mixtures.

Table 2  
Values of  $\lambda_{\max}$  and  $A_e$  of the PC form and  $K_e$  of  $2.0 \times 10^{-3} \text{ mol l}^{-1}$  SP-16 in ethanol–acetone mixtures at 31 °C

Solvent	$\lambda_{\max}$ (nm)	$A_e$	$K_e \times 10^3$
Ethanol	543	1.65	23.6
Ethanol(90)–acetone(10)	544	1.69	24.1
Ethanol(80)–acetone(20)	544	1.65	23.6
Ethanol(70)–acetone(30)	545	1.53	21.9
Ethanol(50)–acetone(50)	546	1.35	19.2
Ethanol(40)–acetone(60)	547	1.16	16.5
Ethanol(30)–acetone(70)	549	0.950	13.6
Ethanol(20)–acetone(80)	552	0.702	10.0
Ethanol(90)–acetone(10)	559	0.451	6.44
Acetone	571	0.270	3.86

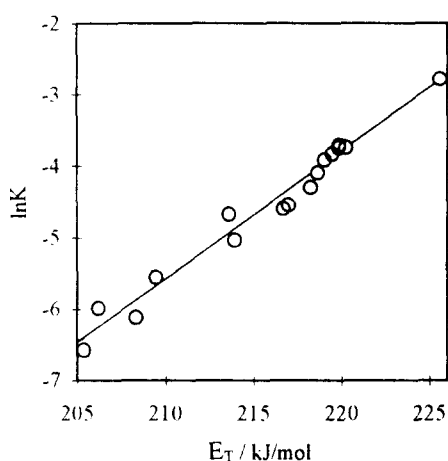


Fig. 2. Plot of  $\ln K_e$  vs.  $E_T$ .

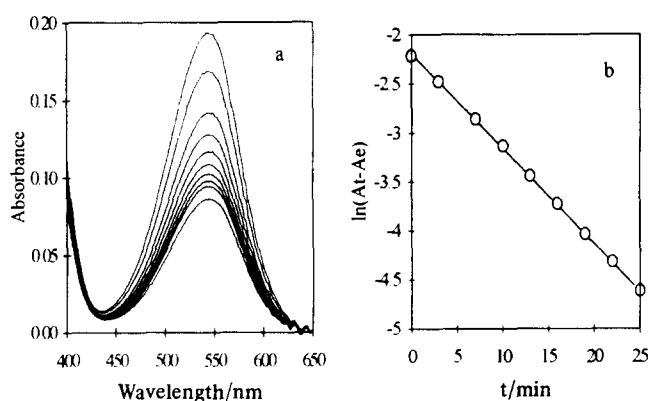


Fig. 3. (a) Variation of the visible spectrum of the photoinduced coloured form of SP-16 in ethanol. Time (min): 0, 3, 7, 10, 13, 16, 19, 22, 25,  $\infty$ . (b) Rate constant plot for first-order decolouration.

### 3.2. Intramolecular Lewis acid–base equilibrium

Usually, a freshly prepared concentrated solution of SP-16 is colourless at room temperature; it is converted into its isomeric form and colours slowly in the dark until an equilibrium is established. The equilibrium is a typical intramolecular Lewis acid–base equilibrium [11]. The position of

this equilibrium, shown in Scheme 1, depends mainly on the different degree of solvation of PC and SP.

Using Eq. (1), the equilibrium constant  $K_e$  can be obtained (Tables 1 and 2). As the polarity of the solvent increases, the corresponding  $K_e$  value increases. This implies that the polarity of SP is lower than that of PC. Thus with an increase in the polarity of the solvent, the decrease in the Gibbs energy of PC by solvation is larger than that of SP [11].

In order to determine quantitatively the effect of the solvent on the intramolecular Lewis acid–base equilibrium, the solvation energy of PC is considered to be varied as the solute molecule is modified by certain substituents. The spectroscopic Hammett equation, first introduced by Kosower et al. [12] for describing the effect of substituents on the spectral shift, is used

$$\frac{E_{T,X} - E_{T,O}}{RT \ln 10} = \sigma \Theta_A \quad (4)$$

where  $E_{T,X}$  and  $E_{T,O}$  are the transition energies, in kilojoules per mole, of the PC form in the solvent concerned and the reference solvent respectively,  $\sigma$  is the Hammett constant of the solvent concerned, similar to the Hammett constant for the substituents, and  $\Theta_A$  is the absorption constant.

Similarly, if the Hammett equation [13] is used to treat the equilibrium or rate constants in different solvents, we have

$$\log(k_X/k_0) = \sigma \Theta \quad (5)$$

where  $k_X$  and  $k_0$  are the equilibrium or rate constants of the reaction studied in the medium concerned and the reference medium respectively.

By comparing Eqs. (4) and (5), we have

$$\log(k_X/k_0) = \frac{\Theta}{\Theta_A} \frac{E_{T,X} - E_{T,O}}{RT \ln 10} \quad (6)$$

or

$$\ln K_X = m E_{T,X} + C \quad (7)$$

where

$$m = \frac{\Theta}{\Theta_A RT}, \quad C = \ln K_0 - \frac{\Theta E_{T,O}}{\Theta_A RT}$$

By fitting the data given in Tables 1 and 2 to Eq. (7), Fig. 2 is obtained. The regression equation for the linear relation is

$$\ln K_e = 0.180 E_T - 43.5 \quad (n = 16, r = 0.984) \quad (8)$$

### 3.3. Photochromism

In the organic media used, a dilute solution of SP-16 is colourless or slightly coloured. On UV irradiation, it displays “normal” photochromism, i.e. the spirobenzopyran molecule in the SP form is converted to the PC form and then regenerates thermally in the dark. Fig. 3(a) shows the vari-

Table 3  
Absorption maxima and rate constants of thermal decolouration of PC in ethanol–acetone mixtures and neat organic solvents at 31 °C

Solvent	$\lambda_{\max}$ (nm)	$k_{dc} \times 10^3$	$\ln k_{dc}$
Ethanol	543	1.59	-6.44
Ethanol(90)–acetone(10)	544	1.67	-6.40
Ethanol(80)–acetone(20)	544	1.61	-6.43
Ethanol(70)–acetone(30)	645	1.79	-6.33
Ethanol(50)–acetone(50)	546	1.83	-6.30
Ethanol(40)–acetone(60)	547	2.01	-6.21
Ethanol(30)–acetone(70)	549	2.40	-6.03
Ethanol(20)–acetone(80)	552	3.02	-5.80
Ethanol(10)–acetone(90)	559	4.17	-5.48
Acetone	571	1.07	-4.54
2-Propanol	551	2.54	-5.97
Acetonitrile	560	4.61	-5.38
1,2-Dichloroethane	580	23.1	-3.77
Butanone	574	10.4	-4.56
Tri- <i>n</i> -butylphosphate	582	19.8	-3.92

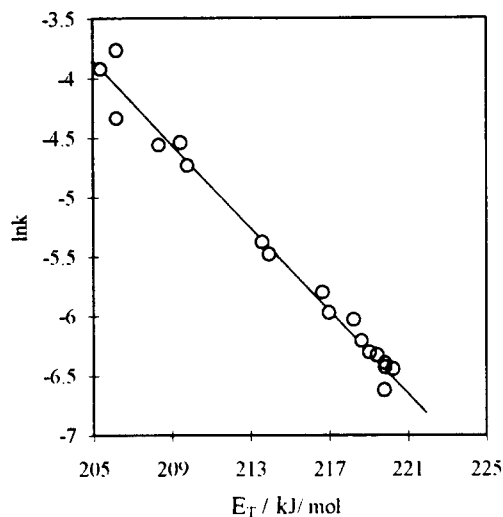


Fig. 4. Plot of  $\ln k_{dc}$  vs.  $E_T$ .

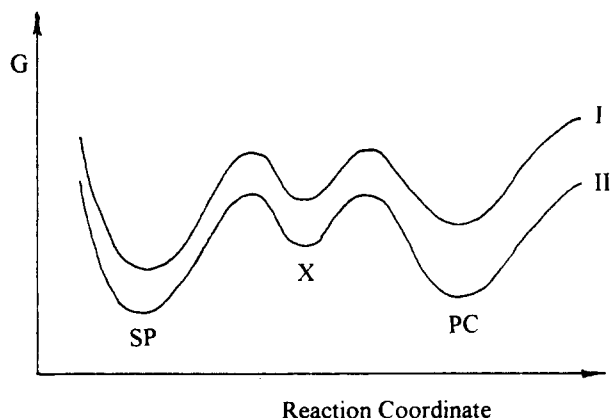


Fig. 5. Potential energy surfaces for the colouration and decolouration pathways of spiropyran in two different solvents I and II (polarity II > polarity I).

ation of the visible absorption spectrum of the PC form of SP-16 in ethanol after UV irradiation as a function of time. By fitting the data from Fig. 3(a) into Eq. (2), it can be seen that the decolouration process may be formulated by first-order kinetics as expected (Fig. 3(b)).

From Fig. 3(b), the rate constant of the decolouration process can be obtained. Similarly, the decolouration rate constants  $k_{dc}$  of the PC form in other neat organic solvents and ethanol–acetone mixtures can be obtained and are listed in Table 3.

To determine quantitatively the effect of the solvent on the decolouration process, Nadolski et al. [14] have suggested that there is a linear relationship between the free activation energy for decolouration and the electronic transition energy of PC. In the recent work of Keum et al. [15], a linear relationship between  $\ln k_{dc}$  and  $E_T(30)$  of the solvents was observed. However, in Ref. [15], hydrocarbons and other low polarity solvents were used. From the spectra in Ref. [15], it can be seen that part of the PC form exists as aggregates in low polarity solvents [16]. Therefore difficulties will be encountered in the measurement of the decolouration rate constant and electronic transition energy. In the present work, polar solvents were used so that the formation of aggregates could be avoided completely. Treating the data in Table 3 using Eq. (7), the relation between  $\ln k_{dc}$  and  $E_T$  (Fig. 4) is obtained and expressed as

$$\ln k_{dc} = -0.178E_T + 32.6 \quad (n = 15, r = 0.993) \quad (9)$$

### 3.4. Mechanism of decolouration and colouration process

Several mechanisms have been proposed to interpret the ring-opening reaction of SP or the ring-closing reaction of PC, e.g. the concerted electrocyclic mechanism suggested by Ollis et al. [17] and Dürr [2]. According to this mechanism, an isopolar, six-membered, activated intermediate is formed in the reaction and the reaction is not sensitive to the medium polarity. In the present case, the ring-opening rate constant of SP cannot be measured directly. However, the values in different solvents and the effect of solvent polarity can be determined in the following way.

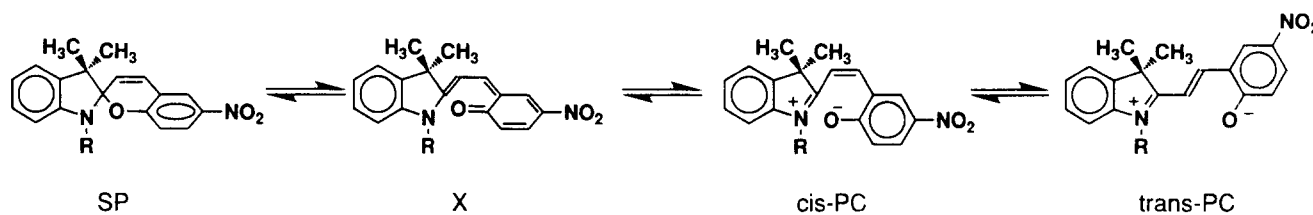
$$\text{Since } K = k_{op}/\{k\}_{dc}$$

$$\ln K = \ln k_{op} - \ln k_{dc} \quad (10)$$

or

$$\ln k_{op} = \ln K + \ln k_{dc} = 0.003E_T - 10.9 \quad (11)$$

From Eq. (11), it is obvious that the effect of the solvent polarity on the ring-opening rate of SP in the dark is negligibly small. Such a result is consistent with the concerted electrocyclic mechanism. However, from Eq. (9), it can be seen that the decolouration rate constants decrease as the solvent polarity increases. This indicates that the charge density of the activated intermediate is lower than that of PC. This cannot be expected from the concerted electrocyclic mechanism. In the recent work of Keum et al. [15], the ionic



Scheme 2. Interconversion between SP and PC.

decolouration mechanism via a merocyanine-type zwitterionic species, first suggested by Flannery [9], was used to describe the decolouration process. The different solvent dependence of the colouration and decolouration processes can be interpreted in the following way. The interconversion between SP and PC involves an intermediate X [18,19]. In the colouration process, X is formed as the bond between the spiro carbon atom and the pyran oxygen atom is ruptured; the orthogonal topology is retained (Scheme 2). The X form then transforms to the cis and trans PC forms successively. Since the formation of X is an electrocyclic reaction and is the rate-determining step (Fig. 5), the solvent effect is very weak. However, in the decolouration process, the trans–cis isomerization and internal rotation around the olefinic double bond for the formation of X must occur before ring closure can take place. The trans–cis isomerization and internal rotation are considered to be sensitive to the solvent polarity and are the rate-determining steps of the overall reaction. Similar to the introduction of an electron-withdrawing group at the 8' position of the benzopyran moiety [15], the increase in the polarity of the solvent will stabilize the zwitterionic form of PC and increase the  $\pi$  bond order of the olefinic double bond. Accordingly, this makes the internal rotation around the olefinic double bond difficult and leads to a decrease in the decolouration rate.

#### 4. Conclusions

For the spirobenzopyran moiety SP-16, it has been confirmed that the solvatochromism, Lewis acid–base equilibrium and photochromism are similar solvent-dependent processes. The transition energy  $E_T$  of the coloured form can be used to deduce the corresponding Lewis acid–base equilibrium constants  $K_e$  and thermal decolouration rates  $k_{dc}$  of PC in neat and mixed organic solvents by the linear correla-

tions between  $\ln K_e$  or  $\ln k_{dc}$  and  $E_T$ . For the decolouration process, the trans–cis isomerization and internal rotation are solvent polarity sensitive and the rate-determining steps. The relatively small influence of the solvent polarity on the colouration rate  $k_{op}$  can be interpreted by the fact that the rate-determining step in the colouration process is a concerted ring-opening reaction.

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