

Substituent and solvent effect on the photochromic properties of a series of spiroindolinonaphthooxazines

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Abstract

The photochromic reactions of six recently synthesised spiroindolinonaphthooxazines bearing different substituents on the basic skeleton are studied under continuous UV irradiation in solvents of different polarity. A comparison of these results with the data obtained for the unsubstituted parent compound provides the examination of the specific effect of substituents on their photochromic properties and relaxation kinetics. The photomerocyanines of all substituted compounds show positive solvatochromism indicating that their excited state is more polar than the ground state. High colourabilities (up to 8.5×10^4) of photomerocyanines are calculated from the absorbance values obtained by extrapolation to $t = 0$ of their room temperature linearly descending kinetic curves $\ln A/t$. The relaxation time at 25 °C ranges from 2 to 130 s the actual value depending on the compound and solvent.

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1. Introduction

Photochromism is a reversible phenomenon involving photoinduced changes in the visible absorption spectrum. It has attracted much attention because of the wide variety of practical applications of photochromic systems most of which are spiro-compounds [1–18]. Among them, the compounds of the spiroindolinonaphthooxazine series (SO) are a topic of increasing interest because of their good colouring power and photofatigue resistance both providing a potential application in many new technologies such as data recording and storage, optical switching, displays and nonlinear optics [3–18]. These compounds are comprised of two heterocyclic nearly planar moieties (indoline and naphthooxazine) linked by a tetrahedral spiro-carbon which prevents the two π -electron systems from conjugation. As a result, the spiro-compounds are almost colourless or pale yellow since the lowest electronic transition of the molecule occurs in the near UV region.

The photochromism of these molecules is due to a photo-cleavage of the C–O spirobond according to Scheme 1

under UV irradiation and subsequent rotation about C–C bond to give an open merocyanine (MC) structure (photomerocyanine) which absorbs in the visible region and the molecule is intensively coloured. The merocyanine is represented here by its *trans–trans–cis* (TTC) conformation [19,20]. When irradiation is stopped, the solution returns thermally to the original state.

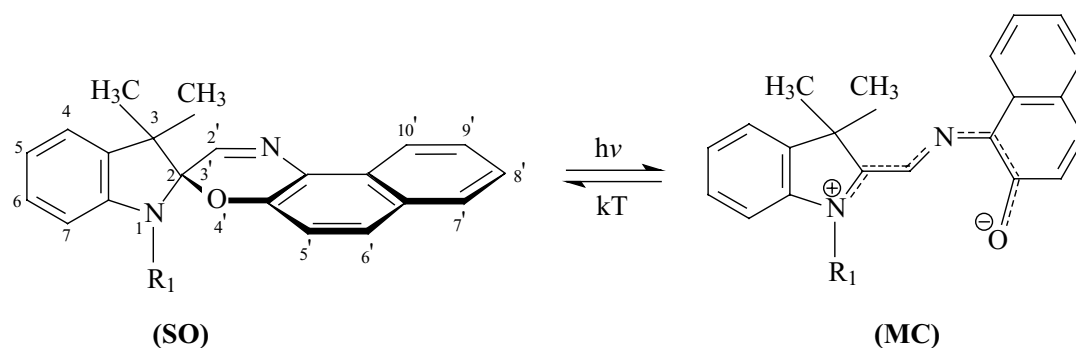
In this paper we report the effect of solvent and structure on the absorption properties and kinetics of thermal bleaching of the photomerocyanines of several recently synthesised in our laboratory spiroindolinonaphthooxazines [21] with selected substituents both in the naphthooxazine and indoline ring systems. The investigation involves the basic unsubstituted spirooxazine compound and six derivatives all exhibiting strong colouration which is considered important for practical applications. The chemical structures of compounds studied are given in Fig. 1.

2. Materials and methods

2.1. Materials

The molecules under study were seven spiroindolinonaphthooxazines: 1,3,3-trimethyl(indoline-2,3'-[3H]naphtho-

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Scheme 1.

[2,1-b][1,4]oxazine) (**0**); 1,3,3-trimethyl-5-hydroxyspiro(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (**1**); 1-butyl-3,3-dimethyl-5'-hydroxyspiro(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (**2**); 1,3,3-trimethyl-5'-(2-benzothiazolyl)-spiro(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (**3**); 1-butyl-3,3-dimethyl-5'-(2-benzothiazolyl)-spiro(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (**4**); 1,3,3-trimethyl-5'-(2-benzothiazolyl)-spironaphth(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (**5**); and 1-butyl-3,3-dimethyl-5'-(2-benzothiazolyl)-spironaphth(indoline-2,3'-[3H]naphtho[2,1-b][1,4]oxazine) (**6**).

Compounds **0–6** were recently prepared and characterised in our laboratory [21]. The solvents were used after distillation.

2.2. Instrumentation

A 250 W medium-pressure mercury lamp housed in a light box was used for producing the coloured form and its absorption spectrum was recorded with an Ocean Optics PC2000 fast scanning spectrometer capable of recording the

whole absorption spectrum in the visible region in 10 ms in an 1 cm quartz cell. The photochemical reactions were carried out in the spectrophotometric cell. The irradiation was performed in the spectrophotometer holder at right angles to the monitoring beam. The light was homogeneously spread on the cell window to avoid stirring [11,16]. The measurements were made on aerated solutions at room temperature.

2.3. Kinetic measurements in solution

The general procedure for determination of the fading kinetics of the photomerocyanines was as follows.

A solution of the spiro-compound in the appropriate solvent, with a concentration sufficient to give an absorbance of ca. 0.8–1.0 at the corresponding λ_{\max} was exposed to UV light in a quartz cell until the colour was fully developed. Trial and error experiments enabled the optimum exposure time to be determined for maximum build-up of the photomerocyanine concentration. The thermal decay was then recorded after the photoequilibration was obtained by closing the shutter (zero time).

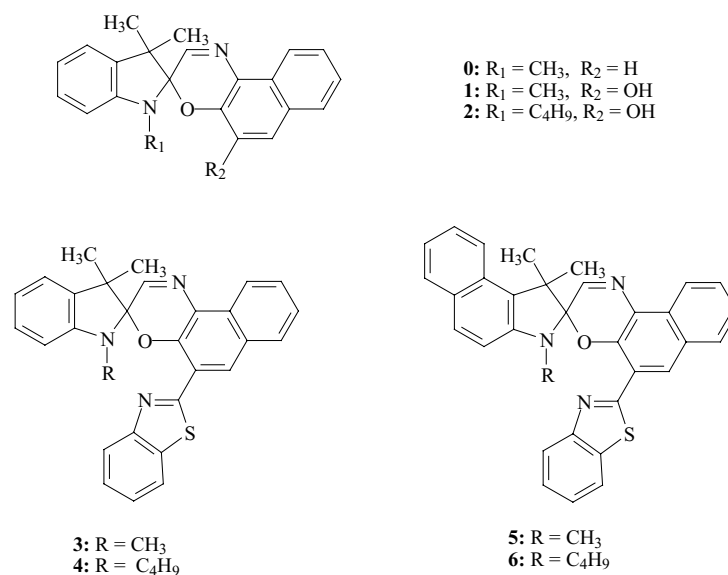


Fig. 1. Chemical structure of compounds studied.

The kinetic rate parameters of the ring closure reaction were determined following the disappearance of the coloured form at the wavelength of maximum absorbance starting 1–2 s after the end of irradiation. First order rate constants k were calculated from linear $\ln A$ versus time plots, where A was the absorbance at λ_{\max} measured at t .

3. Results and discussion

3.1. Absorption spectra

The electronic absorption spectra of the colourless spiro forms consist of localised π – π^* transitions in the UV region, belonging to the two orthogonal halves of the molecule. The long-wave absorption bands close to 320 and 340 nm in the UV spectrum of the parent unsubstituted spiroindolinonaphthooxazine (**0**) in hexane are associated with the oxazine part of the molecule in its closed form. They correspond well to the previously reported data [7] about the same compound in ethanol. The UV spectra of substituted compounds are substantially different [21], since –OH derivatives **1** and **2** exhibit a broad UV absorption about 345 nm while benzothiazolyl substituted compounds **3–6** have a large number of narrow absorption bands in the region 270–340 nm formed by electronic and vibronic transitions, localised on the naphthooxazine fragment of the molecule.

The visible spectra of photomerocyanines **0–6**, obtained by UV irradiation in solvents of different polarity, are characterised by a strong absorption band in the range 560–660 nm (Table 1). According to data of Table 1 addition of –OH at the 5' position in the naphthooxazine moiety has a minor effect on the visible band of the MC derived from compounds **1** and **2** compared to the parent **0**. The effect of benzothiazolyl substituent at the same position reveals a moderate bathochromic shift of 30 to 65 nm in the spectrum of the MC derived from compound **3**. Replacing benzene in the indoline moiety with naphthalene additionally shifts by 15–20 nm to longer wavelength the visible band of the MC derived from compounds **5** and **6**. Replacing the –CH₃ group on the nitrogen in the indoline part of the molecule with –C₄H₉ group has practically no effect on the visible absorption.

Visible spectra of photomerocyanines derived from compounds **0** and **3–6** are apparently not single absorptions, but show in each case shorter wavelength shoulder of the main absorption band (Fig. 2), like the spectra of other photomerocyanines of this type [7,10,12,13,18,22]. Visible spectra of

1 and **2** reveal only a wide single absorption band (Fig. 3).

“Colourability” [8,11,18,23] of photomerocyanines was calculated from the absorbance A_0 obtained by extrapolation to $t = 0$ of the room temperature linearly descending kinetic curves $\ln A/t$ (Figs. 4 and 5) taken immediately after UV-irradiation. The values of A_0/cl are given in Table 1. When measured in this way “colourability” depends on the quantum yield φ_c of the colour-forming reaction and the ε -value of the visible absorption band.

The bathochromic shifts observed in Table 1 at higher solvent polarity, positive solvatochromism, are indicative of a better stabilisation of the excited state of the photomerocyanines relative to the ground state, i.e. of an increasing dipole moment upon electronic excitation. Therefore, the ground-state weakly polar molecule should approach the configuration of the quinoid form and the excited state should have a prevalent zwitterionic character. However, there is not a direct correlation between the bathochromic shift observed and the polarity of the solvent. The high “colourability” of the visible absorption band and the observed bathochromic shift of the spectrum at higher polarity of the medium are consistent with the π – π^* character of the singlet excited state of the open form [17].

In addition to the solvatochromic effect, a change in solvent also affects the thermal equilibrium between the closed and the opened forms. Polar solvents promote the formation of the coloured forms at room temperature in the absence of light. However, the opened form can be detected even in the most unfavourable conditions (i.e. unsubstituted spirooxazine compound **0** in hexane) at concentration of ca. $5 \times 10^{-3} \text{ mol dm}^{-3}$. The coloured merocyanine forms, either photoinduced or arising from the solvation effect, are spectroscopically identical. Fig. 2a depicts the visible absorption spectral changes of **6** upon UV-irradiation of $1 \times 10^{-5} \text{ mol dm}^{-3}$ hexane solution. The original spectral pattern is reversibly recovered within few seconds in the dark (Fig. 2b). The new band is ascribable to the generation of the open merocyanine form from the closed spiro form.

A relevant representation of the visible spectral changes obtained upon UV-irradiation of $2.5 \times 10^{-5} \text{ mol dm}^{-3}$ of **1** in acetonitrile is given in Fig. 3a and b. Spectra measured after UV irradiation are proportional to each other in the visible region, indicating that only one species is formed. This allows the absorption to be monitored at λ_{\max} as a function of time to obtain the thermal colour fading rate constant (k) of the transformation from the open merocyanine form to the closed spiro form.

Table 1

Experimental values of λ_{\max} (nm) and “colourability” ($\times 10^{-4}$) of the visible absorption of the photomerocyanines derived from compounds **0–6**

Solvent	0	1	2	3	4	5	6
Hexane	560 (4.55)	565 (6.87)	570 (6.96)	625 (6.61)	630 (6.84)	642 (6.46)	648 (7.25)
Acetone	600 (5.50)	590 (4.27)	595 (4.37)	640 (5.89)	642 (7.25)	655 (6.76)	656 (7.28)
Acetonitrile	600 (6.92)	595 (5.79)	597 (5.88)	640 (6.19)	645 (6.98)	658 (7.08)	658 (7.24)
Ethanol	610 (5.25)	600 (5.94)	605 (6.32)	642 (7.10)	648 (8.45)	660 (6.82)	660 (8.02)

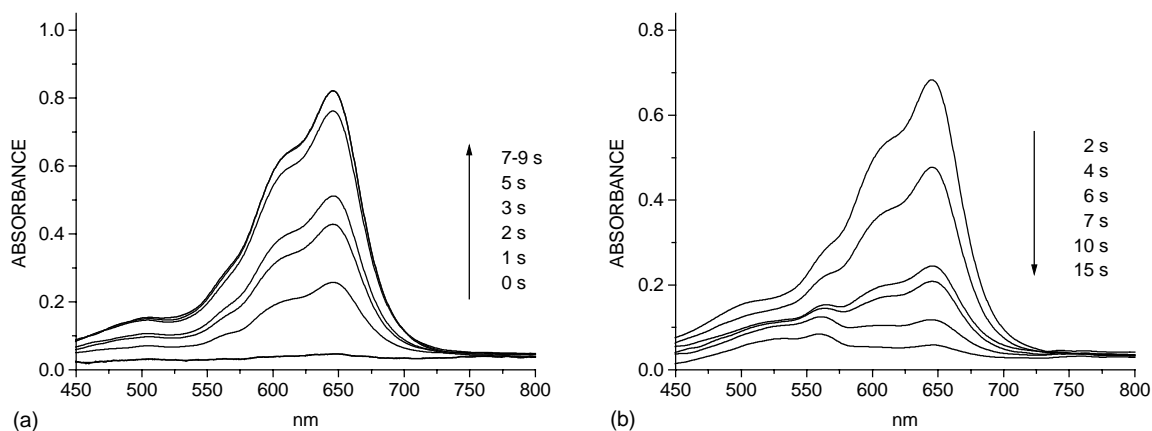


Fig. 2. Visible absorption spectra of 1×10^{-5} M hexane solution of **6** taken: upon 0, 1, 2, 3, 5 or 7–9 s UV irradiation (a) and on keeping the irradiated sample for 2, 4, 6, 7, 10 and 15 s in the dark (b).

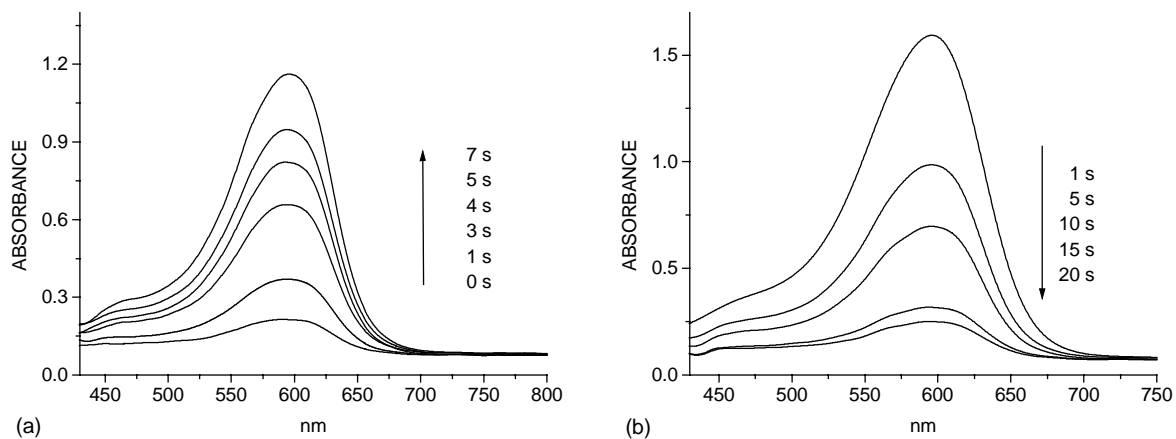


Fig. 3. Visible absorption spectra of 2.5×10^{-5} M acetonitrile solution of **1** taken: upon 0, 1, 3, 4, 5 or 7 s UV irradiation (a) and on keeping the irradiated sample for 1, 5, 10, 15 and 20 s in the dark (b).

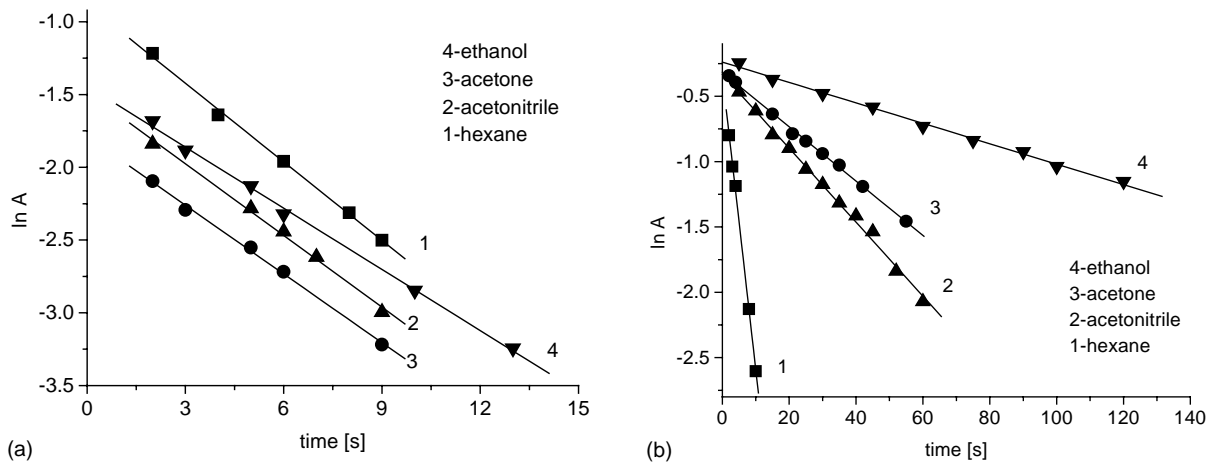


Fig. 4. Kinetic runs ($\ln A$ vs. time) at 600 nm after irradiation of 1×10^{-5} M solutions of **1** (a) and **6** (b) in solvents of different polarities.

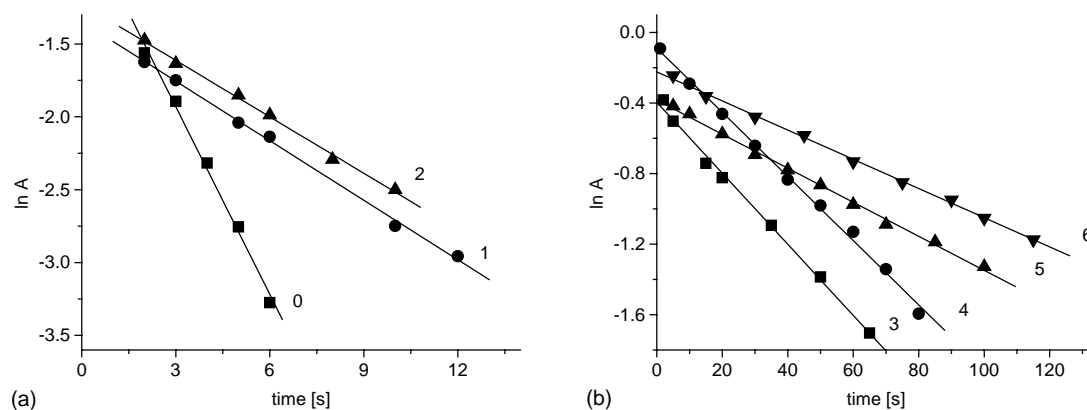


Fig. 5. Kinetics runs ($\ln A$ vs. time) at 600 nm after irradiation of 1.10^{-5} M solutions of **0–2** (a) and **3–6** (b) in ethanol.

3.2. Thermal fading kinetics of the photomerocyanines in solution

Kinetic runs followed immediately after irradiation of **1** or **6** in a range of solvents of different polarity (Fig. 4a and b) show that the thermal ring closure reaction follows first order kinetics in the concentration of the photomerocyanine as plots of $\ln A/t$ are linear. The slopes of the $\ln A/t$ lines gave the first order rate constants, k . Similar strongly descending curves associated with the thermal ring closure of the other obtained photomerocyanines at 20 °C in solvents of different polarities were also analysed by the least squares method to give the results of k in Table 2. The relaxation time of the photomerocyanines (τ_{MC-SO}) given in Table 2 was obtained from the first order rate constant using the expression $\tau = 1/k$.

Kinetic runs in Fig. 4a indicate a relatively slower decrease of absorbance in ethanol and slightly faster decrease in hexane. In acetone and acetonitrile time dependence of absorbance decrease is very similar. Thus, data in Fig. 4a do not show any noticeable dependence of the rate of cyclization of photomerocyanine derived from $-OH$ derivative **1** on the solvent polarity and the same is observed about compound **2** and the parent unsubstituted compound **0** in Table 2. In opposite, data in Fig. 4b show that the nature of the solvent has a significant effect on the rate of cyclization of photomerocyanine derived from benzothiazolyl-substituted compound **6** and similar results are obtained about compounds **3–5** in Table 2. Thus, ethanol provided an example of a protic polar solvent, acetone and acetonitrile of polar aprotic solvents,

and hexane, a non-polar aprotic solvent. In hexane, the merocyanine receives little solvent stabilisation and cyclization is rapid, whereas in acetone and acetonitrile, relatively higher stabilisation of the polar merocyanine compared to the non-polar spiro-compound is the reason of slower cyclization. The effect is quite pronounced in ethanol, where decolouration reaction is up to 30 times slower than in hexane most probably due to the combined effect of stabilisation of the polar merocyanine and its specific solute-solvent interaction like hydrogen bonding with ethanol.

Kinetic runs illustrating the effect of different substituents on the colour fading of photomerocyanines in ethanol are depicted in Fig. 5a and b. The corresponding values of k and τ_{MC-SO} are given in Table 2. According to these values addition of $-OH$ at the 5' position in the naphthooxazine moiety only slightly increases the relaxation time of photomerocyanines derived from compounds **1** and **2**, the effect being better pronounced in ethanol. Addition of benzothiazolyl substituent at the same position has stronger effect on the rate of cyclization and the value of τ_{MC-SO} of the photomerocyanine derived from compound **3** is up to 25 times larger than that obtained for the parent unsubstituted compound **0**. The rate of reversion of photomerocyanines derived from compounds **5** and **6** is additionally (about twice) decreased on replacing benzene in the indoline moiety by naphthalene. The rate of thermal relaxation is unaffected on changing the N -alkyl group on the indoline part of the molecule from $-CH_3$ to $-C_4H_9$ group.

The obtained results definitively show that τ_{MC-SO} values vary gradually for **0–6** depending both on structural

Table 2

Rate constants k ($\times 10^2$ s $^{-1}$) of thermal ring closure of photomerocyanines derived from compounds **0–6** and their lifetimes τ_{MC-SO} (s)

Solvent	0	1	2	3	4	5	6
Hexane	52.5 (2)	18.0 (5)	18.7 (5)	18.0 (5)	18.4 (5)	25.2 (4)	22.5 (4)
Acetone	44.7 (2)	16.8 (6)	15.9 (6)	5.4 (19)	5.1 (20)	2.5 (40)	2.1 (48)
Acetonitrile	54.6 (2)	15.3 (6)	14.2 (7)	5.2 (19)	5.7 (18)	3.3 (30)	2.8 (36)
Ethanol	42.9 (2)	13.6 (7)	12.9 (8)	2.0 (50)	1.9 (53)	1.0 (100)	0.8 (125)

characteristics and solvent polarity. Rather long relaxation time in ethanol is probably due to hydrogen bonding with the open merocyanine form.

The resistance of our compounds to photodegradation (fatigue resistance) is measured by UV irradiation in hexane. We have found that the loss of photochromic response followed spectrophotometrically is accompanied by yellowing phenomenon previously reported and attributed to photooxidation [24].

4. Conclusions

The photochromic properties of the parent spiroindolinonaphthooxazine are modulated by introduction of substituents in different positions of the molecular framework. Thermal ring closure reaction is strongly suppressed when benzthiazolyl substituent is attached to the 5' position in the naphthooxazine moiety and benzene is replaced by naphthalene in the indoline fragment. The combined effect of both substituents could be assigned to a decreased rotational freedom upon cyclization. The effect is enhanced in polar solvents because of the relatively higher stabilisation of the polar merocyanine compared to the non-polar spiro-compound. Thereby, the relaxation time (τ_{MC-SO}) at 25 °C ranges from 2 s for **0** in all solvents to 130 s for **6** in ethanol. High "colourability" values (up to 8.5×10^4) suggest high effectivity of the colour-forming reaction. As a rule, substituents have stronger influence than the solvent and provide an active method of tuning and designing new photochromic molecules.

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