

Solvatokinetic and Solvatochromic Behavior of Bis(indolinobenzospiropyranyl) Sulfide Derivatives in Various Solvents

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Solvatokinetic and solvatochromic behavior of bis(indolinobenzospiropyranyl) sulfide derivatives **1a-1c** have been studied in various solvents. The marked negative solvatochromism is exhibited for **1a** and **1b** in the whole region of solvent polarity examined. Whereas, it is found only in the polar solvent region ($E_T > 37$) for **1c**. The sensitivity order to the solvent media (slope values) is **1a** > **1b** > **1c**. The branched linear plot with a zero slope was shown for the most sterically-hindered compound **1c** in the less polar-solvent region ($E_T < 37$). The biphasic plot is indicative of dual mechanistic process, *i.e.*, a transition state with increased zwitter-ionic character in more polar solvents and electrocyclic process with an isopolar transition state in less polar solvents.

Key Words : Solvatokinetic and solvatochromic behavior, Thermo- and photochromic dyes, Bis(indolinobenzospiropyranyl) sulfides. Dual mechanistic process. Biphasic plot

Introduction

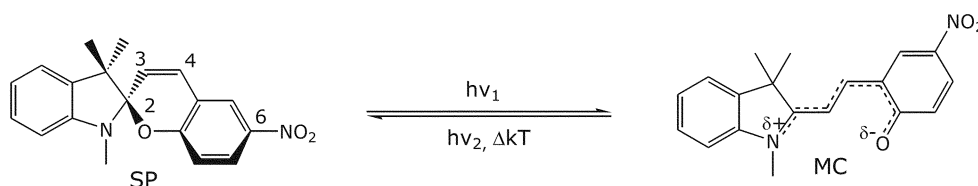
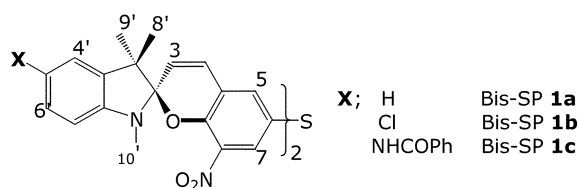
Thermo- and photochromic indolinobenzospiropyran dyes recently have become important in connection with the rapid development of information recording systems, such as high-density optical data storage, optical switching, displays and non-linear optics.^{1,2} Structurally, spiropyran dyes consist of two π systems linked by a tetrahedral spiro carbon. They form a coloured metastable state on heating or irradiation with UV light, while the reverse process is induced by visible light, heat or spontaneously.^{1,2} The metastable state is called *photomerocyanine*, as it resembles the structure of merocyanine dyes (MC). The process is shown in Scheme 1.

Since the stability of the spiropyran structure, as well as the ultimate absorption associated with the merocyanine chromophore, is strongly dependent on the substituents present, it is of interest to investigate the influence of structural changes of the parent spiropyran. Structural modification of spiropyrans has thus been an active area of research.

A major effort in this laboratory has been in the structural modification of spiropyrans for special functionalities.⁵⁻¹² We previously reported the synthesis and characterization of the symmetric and unsymmetric bis-indolinospirobenzopyrans

(BSPs) which contain two spiropyran moieties connected at each of the C-6, either directly or through an alkyl- or arylamido group.^{6,8,12} Since two merocyanine chromophores in the dimeric spiropyran systems were linked either directly or through a connecting group, the two merocyanine chromophores were expected to overlap each other and hence to give bathochromic shift of their maximum wavelengths.

In this connection, structural modification was extended to sulfide derivatives which are also expected to have a potent chiral center on sulfur atom modifying them to a chiral sulfoxide derivatives. Few of thermo- and photochromic bis(spiropyranyl) sulfides are reported so far. In this paper, we describe solvatokinetic and solvatochromic behaviors of bis(indolinobenzospiropyranyl) sulfide derivatives, **1a-1c**, in various solvents.



Scheme 1. Photochromism of 6-nitrospiropyran.

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Experimental Section

General. Melting points were determined using a Fischer-Jones melting point apparatus and are uncorrected. ^1H nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AMX-500 spectrometer in deuterated chloroform. UV-Vis absorption spectra were recorded using a Varian Cary 1E UV-visible spectrometer and IR spectra were recorded using an Analet Instrument FT-IR (MAP-60) using KBr pellets. Photoirradiation was carried out by using a mercury lamp (Ushio, 1 kW) as the excitation light source. Electron Impact (EI) mass spectra were recorded on a Shimadzu GCMS-QP1000 spectrophotometer.

Materials. The required 4,4'-thiodiphenol, Fischer base and 5-chlorinated Fischer base were purchased from Aldrich and were used without further purification. 5-Benzoylamino Fischer's base was prepared according to the known method.⁶

5,5'-Thio bissalicylaldehyde 3. To a solution of 4,4'-thiodiphenol **2** (3 g, 13.6 mmol) in 100 mL toluene was added SnCl_4 (0.35 mL, 2.99 mmol) and tributylamine (2.59 mL, 10.9 mmol) under N_2 at room temperature. After refluxing the reaction mixture for 30 min, paraformaldehyde (2.06 g, 65.3 mmol) was added under N_2 atmosphere and the mixture refluxed for 8 hrs. At the end of reaction, solution was neutralized with 2 M HCl. The solution was extracted with EtOAc, dried with MgSO_4 and finally concentrated *in vacuo*. Flash chromatography (EtOAc 20%-hexane 80%, v/v%) and recrystallization from acetone-hexane afforded 0.38 g (10%) of **3** and 1.38 g (41%) of 3-(*p*-hydroxyphenylsulfanyl)salicylaldehyde **4**. The product **4** was obtained as permanent yellow solid. M.p. 157 °C (Lit.¹⁴ 155-157 °C). IR (KBr, cm^{-1}): 1658 (s), 1469 (s), 1275 (s), 1179 (s), 831 (w), 734 (s). ^1H NMR (CDCl_3): δ 6.98 (d, 1H, $J = 8.7$ Hz), 7.52 (d, 1H), 7.59 (s, 1H), 9.83 (s, 1H), 11.04 (s, 1H).

5,5'-Thiobis(3-nitrosalicylaldehyde) 5. To a solution of 5,5'-thiobissalicylaldehyde (0.5 g, 1.83 mmol) in 50 mL acetic acid, was added nitric acid (0.16 mL) slowly, keeping the solution temperature below 15 °C. The reaction mixture was refluxed for 1 hr. The yellow precipitate was filtered and washed thoroughly with water. The yellow solid was dissolved in EtOAc, dried with MgSO_4 and concentrated *in vacuo*. Flash chromatography (EtOAc 20%-hexane 80%, v/v%) and recrystallization from acetone-hexane afforded 0.3 g of **5**. The product **5** was obtained as permanent yellow solid. M.p. 185-186 °C (decomp.). IR (KBr, cm^{-1}): 3262 (s), 1678 (s), 1531 (s), 1355 (s), 1250 (s), 930 (m), 733 (w). ^1H NMR (CDCl_3): δ 8.01 (s, 1H), 8.29 (s, 1H), 10.23 (s, 1H).

Bispiropyranyl sulfides 1a-1c. Bispiropyranyl sulfides **1a-1c** were generally synthesized by the reaction of substituted 5,5'-thiobissalicylaldehydes and Fischer's Base derivatives in 1 : 2.5 mole ratios, according to the known procedure.⁵ A representative example is: To a solution of 5,5'-thiobis(3-nitrosalicylaldehyde) **5** (0.13 g, 0.357 mmol) in 30 mL methanol was added Fischer's base **6** (0.133 mL, 0.75 mmol) and the mixture refluxed for 1 hr. The solution was allowed to cool to room temperature and concentrated *in vacuo*. Flash chromatography (EtOAc 30%-hexane 70%,

v/v%) and recrystallization from acetone-hexane afforded 0.226 g of bis-spiropyran **1a**.

Bis(8-nitroindolinobenzospiropyranyl) sulfide 1a. Compose-green coloured. Yield 94%. M.p. 240 °C (decomp.) IR (KBr, cm^{-1}): 1606 (w), 1529 (s), 1485 (s), 1348 (s), 1271 (s), 1105 (m), 921 (s). ^1H NMR (300 MHz, CDCl_3) δ 1.19 (s, 3H), 1.38 (s, 3H), 2.75 (s, 3H), 5.91 (d, $J = 10.4$ Hz, 1H), 6.54 (d, $J = 7.7$ Hz, 1H), 6.85 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 10.4$ Hz, 1H), 7.07 (d, $J = 7.3$ Hz, 1H), 7.17 (t, $J = 7.7$ Hz, 1H), 7.29 (s, 1H), 7.68 (s, 1H). M.W. 674.77. EI-MS m/z 674 (M^+ , 82%). Anal. calculated for $\text{C}_{38}\text{H}_{34}\text{N}_4\text{O}_6\text{S}$: C, 67.64; H, 5.08; N, 8.30; S, 4.75. Found: C, 67.58; H, 5.12; N, 8.33; S, 4.79.

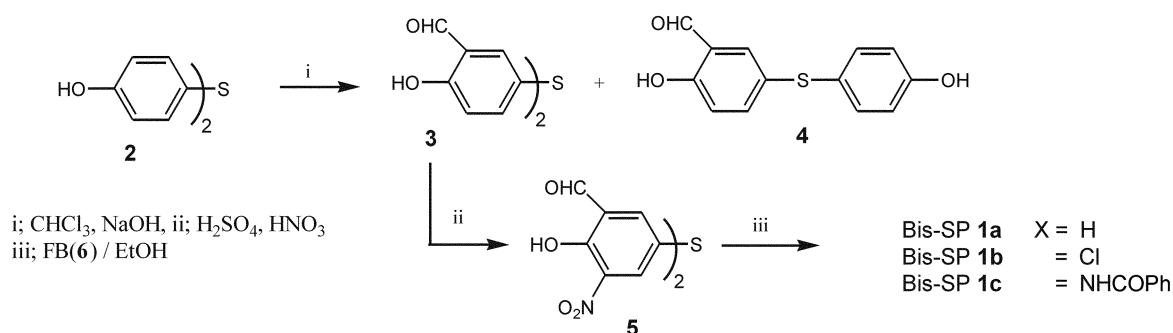
Bis(5'-chloro-8-nitroindolinobenzospiropyranyl) sulfide 1b. Linden-green coloured. Yield 91%. M.p. 248 °C (decomp.) IR (KBr, cm^{-1}): 1602 (m), 1529 (s), 1484 (s), 1346 (s), 1267 (s), 1106 (m), 921 (s). ^1H NMR (300 MHz, CDCl_3) δ 1.19 (s, 3H), 1.33 (s, 3H), 2.75 (s, 3H), 5.91 (d, $J = 10.4$ Hz, 1H), 6.54 (d, $J = 8.3$ Hz, 1H), 6.85 (t, $J = 7.6$ Hz, 1H), 6.88 (d, $J = 10.4$ Hz, 1H), 7.07 (d, $J = 7.3$ Hz, 1H), 7.17 (t, 1H), 7.29 (s, 1H), 7.68 (s, 1H). M.W. 743.65. EI-MS m/z 742 (M^+ , 51%). Anal. calculated for $\text{C}_{38}\text{H}_{32}\text{Cl}_2\text{N}_4\text{O}_6\text{S}$: C, 61.37; H, 4.34; Cl, 9.53; N, 7.53; S, 4.31. Found: C, 61.41; H, 4.36; Cl, 9.58; S, 4.33.

Bis(5-benzoylamino-8-nitroindolinobenzospiropyranyl) sulfide 1c. Prussian blue colored. Yield 76%. M.p. 231 °C. IR (KBr, cm^{-1}): 3417 (s), 1667 (s), 1601 (s), 1527 (s), 1469 (s), 1233 (s), 1110 (w), 956 (w). ^1H NMR (300 MHz, CDCl_3) δ 1.14 (s, 3H), 1.25 (s, 3H), 2.66 (s, 3H), 6.01 (d, $J = 10.4$ Hz, 1H), 6.59 (d, $J = 8.6$ Hz, 1H), 7.17 (d, 1H), 7.46 (s, 1H), 7.50 (d, 1H), 7.56 (s, 1H), 7.70 (s, 1H). M.W. 913.00. EI-MS m/z 912 (M^+ , 11%). Anal. calculated for $\text{C}_{52}\text{H}_{44}\text{N}_6\text{O}_8\text{S}$: C, 68.41; H, 4.86; N, 9.20; S, 3.51. Found: C, 68.31; H, 4.92; N, 9.24; S, 3.56.

Results and Discussion

Synthesis and spectroscopic characterization of bis(8-nitrospiropyranyl) sulfides 1a-1c. Bispiropyranyl sulfides **1a-1c** were generally synthesized by the reaction of 5,5'-thiobis(3-nitrosalicylaldehyde) **5** and Fischer's base derivatives (FB) **6** in 1 : 2.5 mole ratio. For the synthesis of **3**, 4,4'-thiobisphenol **2** in toluene was reacted with SnCl_4 /tributylamine under N_2 , followed by reaction with paraformaldehyde. The formylation of **2** gave the mono-formylated product, hydroxyphenylsulfanyl salicylaldehyde **4** as a major product and the doubly formylated bis-salicylaldehyde **3** as a minor product. Nitration of **3** was performed by reaction with nitric acid/acetic acid to yield **5**.

The IR spectral frequencies of the synthesized bis(8-nitrospiropyranyl) sulfides, **1a-1c**, were obtained using KBr pellets. The Cspiro-O stretching frequencies of **1a-1c** appeared at 921-956 cm^{-1} , as usually found in the indolinobenzospiropyran compounds.^{5,6} The nitro group of the bispiropyrans, **1a-1c** had two strong bands at 1527-1529 and 1346-1348 cm^{-1} , for asymmetric stretching vibration and the symmetric stretching vibration, respectively. Intense



Scheme 2. Preparation of bis(8-nitrospiropyranyl) sulfides **1a-1c**.

aryl C-O stretching absorption was found at 1233-1271 cm⁻¹.

The proton NMR spectral data of the bis(8-nitrospiropyranyl) sulfides, **1a-1c**, in CDCl₃ are given in Experimental section. The proton NMR spectra of these materials showed N-Me peaks at 2.72-2.75 ppm, except for compound **1c** (2.66 ppm, measured in DMSO-*d*₆). Two geminal methyl groups (prochiral center, C3') appeared at 1.15-1.19 ppm and 1.28-1.38 ppm for the 9-methyl and 8-methyl groups, respectively. From the previous *n*Oe experimental study¹⁵ of gem-dimethyl peaks of spiropyran systems, the relative stereochemistry of the indolino gem-dimethyl groups can be assigned. Methyl group C-9' is located close to the olefinic proton H3 and methyl group C-8' is located close to oxygen moiety of the pyranyl group. The olefinic protons appeared as double-doublets at 5.74-5.91 and 6.78-6.95 ppm for H3 & H4, respectively. Their peaks had large coupling constants *J* = 10.2-10.4 Hz for both olefinic protons and the H3 & H4 signals were characteristic of spiropyran systems, as reported previously.¹⁵

Solvatokinetic properties of the bis(spiropyranyl) sulfides 1a-1c. Bis(8-nitrospiropyranyl) sulfides **1a-1c** showed strong chromotropism. The electronic absorption spectra of the spiropyrans in SP state show no absorbance in the visible region, while in MC state, formed on irradiation, a strong absorption at 500-600 nm with a high extinction coefficient is observed. The rate of reversion to the colorless spiro ring (MC → SP) was measured after UV irradiation in various solvents for **1a-1c** by following the disappearance of the absorption band in the 500-600 nm region. The decay rate of the photo-induced colored transients obeyed good first-order kinetics for all substrates examined in this work. Data for the MC → SP conversion in representative solvents (alcohols → ethers) obtained are displayed in Figure 1 in the form of plots of log (rate) vs. the *E*_T(30) solvent polarity parameter. The rate constants are independent of the initial spiropyran concentration in the range of 10⁻³ M to 5 × 10⁻⁵ M.

The rate of the spiro-ring formation is drastically reduced as the solvent polarity is increased. On plotting log (rate) versus the solvent parameter *E*_T reasonably good linear plots were obtained for **1a** & **1b**, as usual.^{1,2,5} Whereas, the biphasic plots derived from the solvatokinetic studies of **1c** were obtained. This is indicative of dual mechanistic process, *i.e.*, a transition state with increased zwitter-ionic

character in more polar solvents and electrocyclic process with an isopolar transition state in less polar solvents, as in some particular cases of mono-spiropyran derivatives.^{16,17} Solvatokinetic properties of the compounds **1a-1c** are summarized in Table 1.

It is apparent that the rate of the ring closure from the open-chain merocyanine form depends markedly on the substituents present in the series **1a-1c**.

Figure 1 shows that there is a fairly good relationship between log (rate) and the solvent polarity parameter *E*_T, with the following relationships:

- [1] Compound **1a**:
Log (rate) = 3.73 - 0.14 *E*_T *r* = 0.988; *n* = 12
- [2] Compound **1b**:
Log (rate) = 1.35 - 0.07 *E*_T *r* = 0.980; *n* = 14
- [3] Compound **1c**:
Log (rate) = 2.97 - 0.13 *E*_T *r* = 0.970; *n* = 9 (*E*_T > 37)

The sensitivity of rate on medium polarity is highest (slope = 0.14) for compound **1a**, which has no substituent in the 5'-position, whereas it is lowest (slope = 0.07) for **1b**, which has a chloro group in the 5'-position.

Another interesting observation is that there is a crossover

Table 1. Ring formation rates of the open chain merocyanine forms of bis(8-nitrospiropyranyl) sulfides in various solvents

Solvent	10 ⁴ <i>k</i> _{obs} (s ⁻¹)			
	<i>E</i> _T	1a	1b	1c
CCl ₄	32.4	2070	884	189
toluene	33.9	823	757	99.9
benzene	34.3	790	810	131
1,4-dioxane	36.0	503	498	224
THF	37.4	375	550	128
Ethyl acetate	38.1	318	480	142
CHCl ₃	39.1	—	281	—
Methyl acetate	40.0	296	554	105
CH ₂ Cl ₂	40.7	180	500	63.1
acetone	42.2	79.3	249	40.2
DMF	43.8	21.3	71.7	13.8
acetonitrile	46.0	24.4	92.2	13.6
2-propanol	48.4	15.7	76.6	6.83
EtOH	51.9	2.37	39.4	0.919

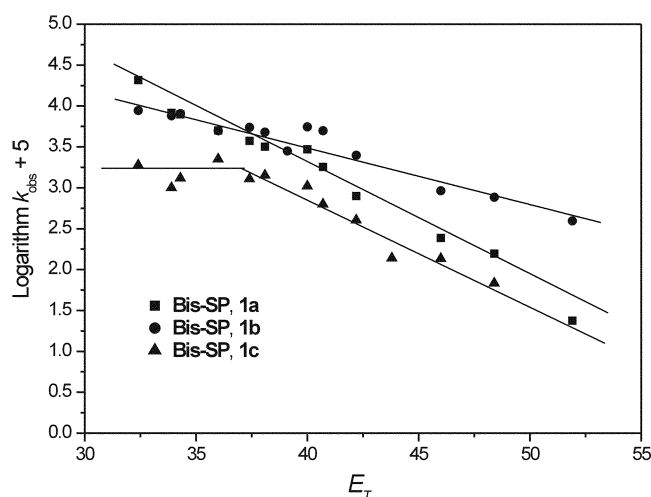


Figure 1. Plots showing correlation between k_{obs} and E_T for the ring-closure reactions of merocyanines from UV irradiation of bis(8-nitrospirobenzopyranyl) sulfides in various solvents: **1a**, (■); **1b**, (●); **1c**, (▲).

in the lines for **1a** & **1b**, while the series **1a** and **1c** exhibit practically parallel lines in the region of above $E_T = 37$. This implies that reactivity comparison studies could be misleading. Thus the order of reactivity will be different in the region below and above $E_T = 37$. If a solvent of relatively low value of E_T is used for the reaction, the reactivity order is **1a** > **1b** > **1c**, whereas for a solvent of higher E_T value the order could be changed to **1a** > **1c** > **1b**.

Solvatochromic properties of the compounds 1a-1c. The UV-VIS spectral data of the open form of the spiro-pyrans **1a**, **1b** and **1c** in various solvents are collected in Table 2, while the results in Figure 2 are plotted as frequency ($\bar{\nu}_{\text{max}}$) versus the solvent polarity parameter E_T .

The results show that a marked solvatochromism^{5,18} is exhibited by the merocyanines derived from spiro-pyrans **1a**,

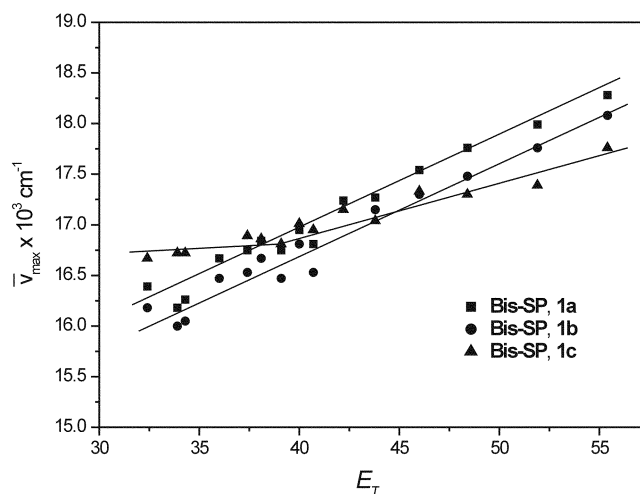


Figure 2. Plots of frequency $10^3 \bar{\nu}_{\text{max}}$ vs. E_T for the open-chain merocyanine form of bis(8-nitrospirobenzopyranyl) sulfides in various solvents: **1a**, (■); **1b**, (●); **1c**, (▲).

1b and **1c**. As the solvent polarity is increased, a hypsochromic shift is observed. Figure 2 shows that there is a fairly good relationship between $\bar{\nu}_{\text{max}}$ and the solvent polarity parameter E_T , with the following relationships:

[1] Compound **1a**:

$$\bar{\nu}_{\text{max}} = 92 E_T + 13270 \quad r = 0.984; n = 15$$

[2] Compound **1b**:

$$\bar{\nu}_{\text{max}} = 90 E_T + 13100 \quad r = 0.980; n = 14$$

[3] Compound **1c**:

$$\bar{\nu}_{\text{max}} = 47 E_T + 15070 \quad r = 0.970; n = 9 \text{ (in } E_T > 37)$$

$$\bar{\nu}_{\text{max}} = 0.04 E_T + 15406 \quad r = 0.973; n = 5 \text{ (in } E_T < 37)$$

The striking feature about the present results, as displayed in Table 2 and Figure 2, is the marked hypsochromic shift that is exhibited with increasing solvent polarity (*i.e.*, negative solvatochromism), for **1a** and **1b** in the whole

Table 2. UV data (λ_{max} , $10^3 \bar{\nu}_{\text{max}}$) of the open chain merocyanine forms of bis(8-nitrospirobenzopyranyl) sulfides in various solvents

Solvent	E_T	1a		1b		1c	
		λ_{max}	$10^3 \bar{\nu}_{\text{max}}$	λ_{max}	$10^3 \bar{\nu}_{\text{max}}$	λ_{max}	$10^3 \bar{\nu}_{\text{max}}$
CCl ₄	32.4	610	16.39	618	16.18	600	16.67
toluene	33.9	618	16.18	625	16.10	598	16.72
benzene	34.3	615	16.26	623	16.05	598	16.72
1,4-dioxane	36.0	600	16.67	607	16.47	587	—
THF	37.4	597	16.75	605	16.53	592	16.89
Ethyl acetate	38.1	594	16.84	600	16.67	593	16.86
CHCl ₃	39.1	597	16.75	607	16.47	595	16.81
Methyl acetate	40.0	590	16.95	595	16.81	588	17.01
CH ₂ Cl ₂	40.7	595	16.81	605	16.53	590	16.95
acetone	42.2	580	17.24	587	—	583	17.15
DMF	43.8	579	17.27	583	17.15	587	17.04
acetonitrile	46.0	570	17.54	578	17.30	577	17.33
2-propanol	48.4	563	17.76	572	17.48	578	—
EtOH	51.9	556	17.99	563	17.76	575	—
MeOH	55.4	547	18.28	553	18.08	563	17.76

region of solvent polarity examined and for **1c** in the polar solvent region ($E_T > 37$). The branched linear plot with about zero slope was shown for the compound **1c** in the less polar-solvent region ($E_T < 37$). The sensitivities to the solvent media (slope values) are 92, 90 and 47 for **1a**, **1b** and **1c**, respectively. These values are relatively lower comparing to those of mono-spiropyran derivatives (ca. 110-140).⁵ It is generally known that the nature of the observed solvent effect for a given dye molecule, i.e., bathochromic or hypsochromic with increasing solvent polarity, depends largely on the change in dipolar characteristics between ground and excited states.¹⁸ For a weakly polar molecule, with low polarity in the ground state and increased polarity in the excited state, a bathochromic shift results. Conversely, for a highly polar molecule in the ground state, a hypsochromic shift is observed. In principle, a merocyanine dye could exhibit either a bathochromic or a hypsochromic shift since the ground state could have an electronic configuration corresponding largely to the nonpolar quinoid form (Qu-form), or to the dipolar, zwitter-ionic form (Zw-form), or an in-between character. The observation of a hypsochromic shift (negative solvatochromism) in the present system is hence indicative of a highly polar ground state, i.e., approaching the configuration of the zwitter-ionic form, and an excited state with decreased polarity. In general terms, we may represent the ground state of the merocyanines as a polyene-like structure and the excited state as a polymethine-like structure, resulting in a hypsochromic shift. Conversely, a bathochromic shift would have the excited state the dipolar structure. Typically, solvatochromic compounds can be described by two extreme resonance-contributing structures: one a quinoidal, nonpolarized, formally nonaromatic structure; the other a zwitter-ionic, polarized, formally aromatic structure.^{18,19} Interaction between two MC chromophores may cause the lower sensitivity toward solvents. The branched solvatochromic behavior with zero slope obtained in the less polar solvent region for **1c** may thus indicate the in-between character in the ground state of **1c**. Similarly, Buncel *et al.*²⁰ has studied extensively the effect of solvent on the rates of ring-closure reaction of N-functionalized merocyanines to spiropyran. It was found that the sterically-hindered MCs possess predominantly quinoid character in nonpolar solvents, whereas the increased zwitter-ionic character of the MCs in polar solvents. The mechanism for ring closure of quinoidal form will be an electrocyclic process, unlikely to an anion-cation recombination in polar solvents, which will be

associated with minimal solvent effect.

In conclusion, the non-branched solvatokinetic behaviors were observed for **1a** & **1b** and the branched behavior for the most sterically-hindered **1c**, as in solvatochromic behaviors. This result may indicate that the ring-closure reaction of **1c** proceed via two different mechanisms: a polar mechanism involving C-O bond cleavage in polar solvents and a nonpolar electrocyclic mechanism in nonpolar solvents.

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