Nonactivated Arylazoindolinobenzospiropyran Derivatives. Part 2[1] : Preparation and Kinetic Measurements of the Spiro-ring Formation from the Merocyanine Form

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Received September 27, 1999

Non-activated indolinobenzospiropyrans, 6-(p-substituted phenylazo)-1',3',3'-trimethylspiroindolinobenzopyrans(**1-4**) have been synthesized by the reaction of commercially available Fischer's base with 2-hydroxy-5-arylazobenzaldehyde (**S1-S4**). The arylazosalicylaldehydes were obtained from the diazocoupling reaction of substituted anilines with salicylaldehyde. The rate of spiro-ring formation from the open form of these nonactivated spiropyran derivatives at room temperature has been investigated utilizing the stopped-flow method developed earlier. Half life times ($t_{1/2}$) of the ring-closure reaction in ethanol are about 0.3-14 seconds for the non-activated spiropyrans examined. UV-Visible absorption spectral data of the open merocyanine form of nonactivated spiropyrans, which showed no chromotropism at room temperature, have also been obtained.

Introduction

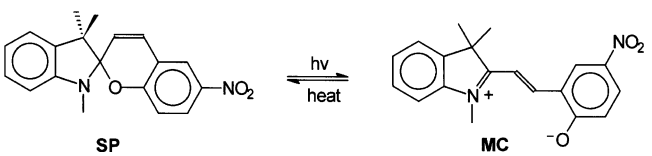
Photochromic indolinobenzospiropyran (spiropyran) dyes have been extensively studied due to their potential applications in many new technologies, including high-density optical data storage, optical switching, displays and non-linear optics.[2,3]

A basic requirement of these systems is that the ring-closed spiropyran (SP) and the open merocyanine (MC) forms should be accessible near ambient temperature through photochemical or thermal interconversion. Due to their propensity to undergo photo- and thermochemical ring opening to a stable merocyanine form, most studies have focused on the activated spiropyran derivatives of 1',3',3'-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2'-indoline].[4-11]

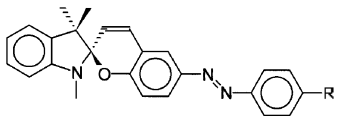
Much less attention has been paid to so-called non-activated spiropyrans, which lack a strong electron-withdrawing group that stabilizes the colored merocyanine form.[12] Upon irradiation, these species give rise to photostationary states with negligible merocyanine concentrations or lack chromotropism, which is undesirable for most photochromic applications. To the nonactivated spiropyrans, the straightforward ultraviolet-visible spectroscopic method to follow the interconversion of SP to MC forms is not applicable. Thus a few studies involving drastic conditions such as laser, flash photolysis or very low temperature have been made so far to monitor the MC-SP equilibrium for the nonactivated systems.[4-6]

Irradiation of a non-activated spiropyran should results in its efficient photoracemization since the merocyanine form is prochiral. If circularly polarized light is used, the photoresolution of a non-activated spiropyran dye should be possible by virtue of circular dichroism (CD).[13] We thus currently began to investigate properties of non-activated spiropyran derivatives in order to develop a ferroelectric liquid crystal optical switch based on the principle of photoresolution.[14]

In order to estimate the theoretical limit for photoresolution of these non-activated spiropyran derivatives, rates of the spiro-ring formation from the open MC form must be determined. In this paper, we report the preparation of the arylazoindolinobenzospiropyrans and kinetic measurements of the spiro-ring formation from the open MC form of **1-4** by the method reported earlier by us.[12]



Scheme 1



R: NO_2 (1), H (2), Cl (3) & N_{nrg} (4)

Experimental Section

General

Melting points were determined using a Fischer-Jones melting point apparatus. ^1H nuclear magnetic resonance (NMR) spectra were obtained in deuterated chloroform on Bruker AMX-500 spectrometer. UV spectra were recorded on a Varian Cary 1E UV-visible spectrometer. Electron Impack (EI) mass spectra were recorded on a Schimazu GCMS-QP1000 spectrophotometer. Osuka Photal RA-401 stopped-flow spectrophotometer was used with a kinetic module. Spectral traces were displayed on the oscilloscope and the data were stored on a transient recorder coupled to a computer to yield pseudo-first order rate constants.

Materials

The azoarylindolinobenzospiropyrans (**1-4**) were prepared from the reaction of azoarylated salicylaldehydes and commercially available Fluka grade Fischer's base, 1,3,3-trimethyl-2-methyleneindoline.

General procedure for the phenyl and pyridylazosalicylaldehydes (S1-S4). Azoarylated salicylaldehydes were generally prepared by the diazocoupling reaction of substituted anilines (or aminopyridines) and salicylaldehyde, according to a previously described procedure.[11] To a solution of correspondingly substituted aniline (25-30 mg, 0.2-0.3 mmol) in HCl (42.7 mg, 0.43 mmol and 10 mL H_2O), a solution of $NaNO_2$ (17.3 mg) in H_2O (10 mL) was added slowly and cooled to 0 °C. The resulting solution was dropped to salicylaldehyde (2.61g) in 20% aq. NaOH (25 mL), keeping temperature at 0 °C. After leaving it to stand for a further 2 h, it was filtered and recrystallized from acetone or aceton/ether. Yields are 84, 78, 86 and 38% for **S1-S4**, respectively.

General procedure for the arylazolindolinobenzospiropyran Derivatives (1-4). Arylazolindolinobenzospiropyran derivatives were obtained from the reaction of Fischer's base and azoarylated salicylaldehydes prepared, according to a previously described procedure.[11] The solution of Fischer's base (26.1 mg, 0.15 mmol) in 10 mL ethanol was poured slowly into an ethanolic solution (20 mL) of azoarylated salicylaldehydes (4-7 mg, 0.18-0.3 mmol) and refluxed for 7 hrs at 60 °C. After reaction was complete, the precipitate was filtered and recrystallized from aceton/ether. Characteristic data for all spiropyrans, **1-4**, prepared are collected in Table 1.

Kinetic measurements

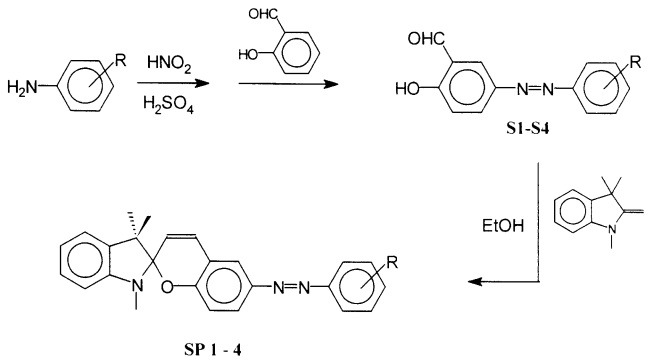
The kinetic method is consisted of acid-induced ring opening of the non-activated spiropyran, followed by neutralization and stopped-flow measurement of ring-closure of the resulting merocyanine.

Acid-induced ring opening. The spiropyran dyes were dissolved in dry DMF (0.1-0.5 mM) and kept in the dark. An aliquot (1-10 mL) was delivered to a quartz cuvette contaning the organic solvent (EtOH). A large excess (10^3-10^4-fold) of HCl was added to a solution of SP to form a protonated salt, SPH$^+$. The appearance of protonated merocyanine form, MCH_{trans+} was followed at wavelength of maximum absorption (430-450 nm).

Stopped-flow measurement. A large excess (10^3-10^4-fold) of HCl was added to a 25 mL volumetric flask containg a solution of SP ($1.0\text{-}2.0 \times 10^{-4}$ mol/L). The solution was allowed to thermally convert into the ring-opened form viz. protonated merocyanine, MCH_{cis+}, slowly, followed by fast isomerization to MCH_{trans+} in the dark for about one hour. The disappearance of MCH_{trans+} was monitored at 595-600 nm by the rapid mixing of the solution of MCH_{trans+} with an ethanol solution containing tri-*n*-butylamine (TBA) (2.0×10^{-3} mol/L) at stopped-flow bench.

Results and Discussion

Preparation of arylazospiropyrans. The arylazospiropyrans were synthesized in 41-72 per cent yield via thermal condensation of azoarylated salicylaldehydes and commercially available Fischer's base, 1,3,3-trimethyl-2-methyleneindoline, as shown in Scheme 2. Azoarylated salicylaldehydes were generally prepared by the diazocoupling reaction of substituted anilines. The characterization including m.p.'s, yields and electron spray (ES) mass spectral data of the synthesized arylazospiropyrans (**1-4**) are given in Tables 1. ^{1}H nmr data including their precursors (**S1-S4**) are collected in Table 2.



Scheme 2

Kinetic method used. Since activated spiropyrans, such as 6'- or 8'-nitro spiropyran derivatives, exihibit very strong chromotropism with concomitant large extinction coefficients for the metastable species, the rate of the spiro-ring closure from the open merocyanine form of SP could be measured directly after UV irradiation. In contrast, nonactivated compounds show either only small coefficients or display no chromotropism at room temperature. As mentioned the straightforward ultraviolet-visible spectroscopic method to follow the interconversion of SP to MC forms is not applicable to the nonactivated spiropyrans, we have thus developed a new kinetic method earlier.[12] The kinetic method used, utilizing stopped-flow spectrophotometric technique, involves two main steps: a protonation-ring opening step in excess acid media and stopped-flow spectrophotometric measurement of the rate of fast ring closure from nonprotonated merocyanine in neutralized media, as shown in Scheme 3.

UV-Visible spectral behavior of spiropyrans in acid. The protonated spiropyran may then thermally convert into the protonated merocyanine form, MCH_{cis+}, followed by fast isomerization into MCH_{trans+}. For a representative example,

Table 1. Characterization of the synthesized arylazospiropyrans (**1-4**)

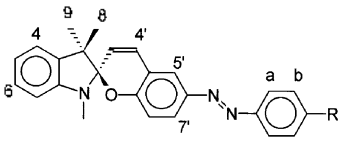
Dye	m.p. (°C)	Colour[a]	Yield (%)	Mw	Molecular ion	
					(m/z)	Relative intensity (%)
1	217	b. red	72	426.5	427.4	100
2	141	y. red	67	381.5	381	100
3	179	yellow	71	415.9	416.3	21.2
4	174	p. yellow	41	382.0	382	100

[a]Solid colour

Table 2. ^{1}H NMR data of the synthesized arylazosalicylaldehydes (**S1-S4**) and arylazospiropyrans (**1-4**) in $CDCl_3$

Dye proton[a]	S1	S2	S3	S4	1	2	3	4
H4	-	-	-	-	7.15	7.52	7.21	7.15
H5	-	-	-	-	6.83	6.78	6.82	6.86
H6	-	-	-	-	7.06	7.12	7.11	7.10
H7	-	-	-	-	6.61	6.69	6.54	6.56
N-Me	-	-	-	-	2.85	2.68	2.75	2.74
8-Me	-	-	-	-	1.37	1.23	1.32	1.35
9-Me	-	-	-	-	1.22	1.11	1.18	1.17
H3'	-	-	-	-	5.66	5.91	5.91	5.79
H4'	-	-	10.0	10.1	6.89	7.20	6.95	6.96
H5'	8.31	8.21	8.20	7.93	7.74	7.80	7.67	7.68
H7'	8.25	8.18	8.18	7.74	7.89	7.83	7.72	7.76
H8'	7.18	7.14	7.14	6.31	6.70	6.87	6.81	6.83
Ha	8.03	7.94	7.50	7.52	8.32	7.71	7.80	7.80
Hb	8.41	7.56	7.86	8.59	7.93	7.55	7.44	7.46
Hc	-	7.51	-	-	-	7.52	-	-
$J_{H3'-H4'}$	-	-	-	-	10.5	10.7	11.3	10.5
$J_{H5'-H7'}$	2.2	2.4	2.4	2.8	2.14	1.96	2.04	2.18
$J_{H7'-H8'}$	8.9	8.6	8.6	9.6	8.16	8.43	8.24	8.63
J_{Ha-Hb}	9.0	-	8.8	6.0	-	-	-	-

[a]The numbering system is following:



Step I: SP $\overset{H^+}{\rightleftharpoons}$ SPH^+ $\xrightarrow[\text{slow}]{k_o}$ MCH_{cis}^+ $\underset{\text{fast}}{\rightleftharpoons}$ MCH_{trans}^+

Step II: MCH_{trans}^+ $\underset{\text{fast}}{\overset{\text{base}}{\rightleftharpoons}}$ MC $\xrightarrow[\text{slow}]{k_c}$ SP

Scheme 3

the UV-Vis spectral behavior of spiropyran, **2**, in excess acidic ethanol is shown in Figure 1. Addition of excess HCl (1.57×10^{-3} mol/L) to a alcoholic solution of **2** (3.52×10^{-5} mol/L) formed new absorption bands at 286 and 360 nm immediatly and a new band at 447 nm, which are expected the absorption band of MCH_{trans}- form of **2**, was grown slowly.

Protonation of SP requires a large excess (10^2-10^3-fold) of acid in organic solvents. Spiropyrans would be expected to be a protonated at either N or O atom of the benzopyran ring in a diffusion-controlled process to form a closed salt, SPH^+. Protonation on azo group (-N=N-) was negligible in the media used since the maximum wavelength of the azoarylated compounds are same as that of non-azoarylated compounds.[12] There is no doubt that the conversion of MCH_{cis}^+ into MCH_{trans}^+ is expected to be very fast since a planar configuration of MCH_{cis}^+ would involve considerable steric interference between N-methylindolinium and phenol moieties. The rotation leads to an apparently less strained conformation, MCH_{trans}^+. Excellent first order linear plots ($r = 0.9997$) were obtained as shown in Figure 1. Half life times of the ring-opening reaction in excess acid are about 40-150 min. for the non-activated spiropyrans examined.

Rates increased as the acid concentration increased at the beginning and then attained at constant values. Rates of ring-opening of protonated spiropyran, **2** as a function of concentrations of acid are shown in Figure 2. The acid concentration was thus chosen in the range of $> 1 \times 10^{-3}$ M in this experiment.

Kinetic rates for the ring-opening of the examined spiropyrans, **1-4**, in excess acidic ethanol are summarized in Table 3. The rates for the ring-opening of **4**, in excess acidic ethanol were 3.50×10^{-3}, 1.10×10^{-2}, 3.02×10^{-2} and 4.57×10^{-2} s^{-1} at 15, 25, 35, & 45 °C, respectively. On plotting Ln k_{obs} versus 1/T for **4** in acidic ethanol, an excellent linear plot was obtained with a slope, -0.918 K and a correlation coefficient, 0.998. The activation energy for the thermal ring-opening reaction of **4** was 11.20 kcal/mol. This value was unusually small compared to 21 and 29 kcal/mol for the 6-nitro and 6-H spiropyrans, respectively.

Kinetic measurement of the ring-closure by stopped-flow spectrometer. The kinetic measurement of the spiro-ring closure from the open form, MCH_{trans}^+ of SP, **1-4** were then performed by stopped-flow spectrophotometer. The disappearance of MCH_{trans}^+ was monitored 595-600 nm by

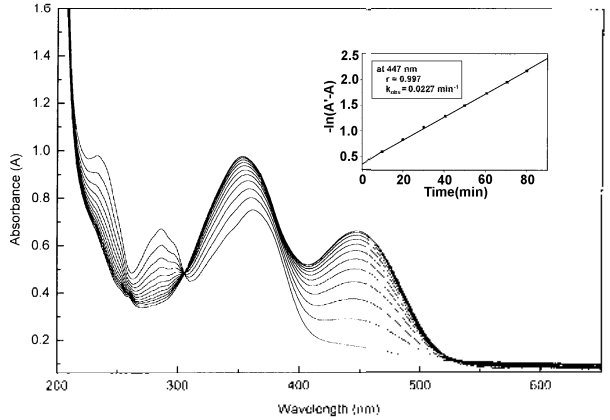


Figure 1. Sample kinetic run for the ring-opening reaction of SP **2** in excess acidic ethanol. (Inlet: a linear plot of ln [**2**] *vs.* time interval).

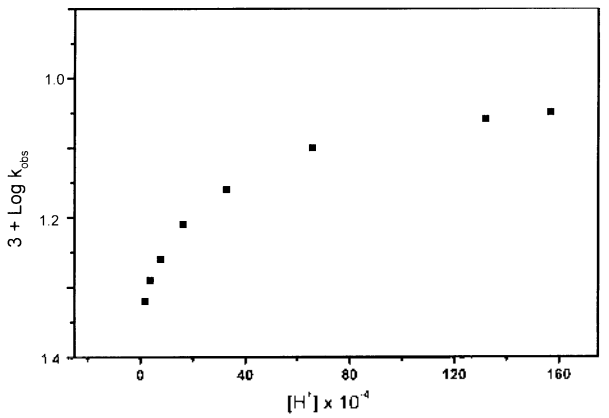


Figure 2. Plot of log k_o versus [H^+] for SP **2** at 445 nm in excess acidic ethanol.

Table 3. Kinetic data for the ring-opening reaction (k_o) in excess acidic ethanol and the ring-closure reaction (k_c) for the non-activated SP, **1-4**

Dye	Substituent (X) in -N=N-Ph-X	Rate (SP → MCH$^+$) $k_o \times 10^{-3}$ ($t_{1/2}$ min.)	rate (MC → SP) $k_c \times 10^{-1}$ ($t_{1/2}$ sec.)
1	p-NO_2	4.68 (150)	234 (0.3)
2	H	8.71 (80)	29.1 (2.4)
3	p-Cl	17.4 (40)	21.9 (3.2)
4	4-N	16.8 (41)	5.00 (14)

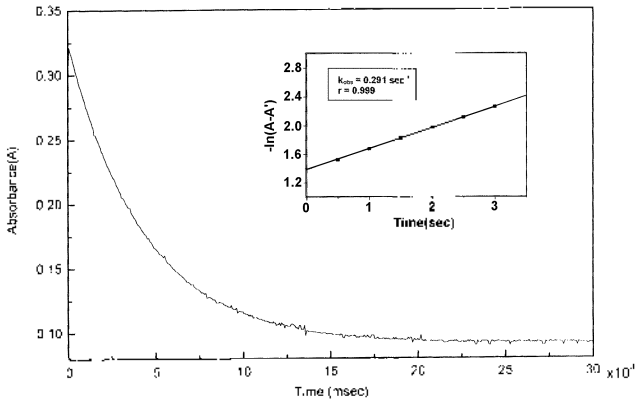
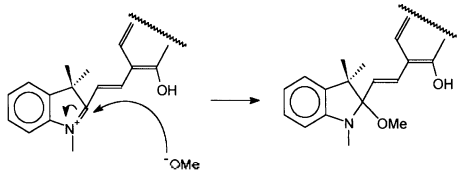


Figure 3. Stopped-flow spectroscopic plot of for the ring-closure reaction of SP **2**. (Inlet: a linear plot of absorbance *vs.* time).

mixing of organic solutions of MCH_{trans}^+ with TBA containing organic solutions at the stopped-flow bench. Excellent first order plots were obtained as shown in Figure 3. Half life times of the ring-closure reaction in ethanol are about 5-6 seconds for the non-activated spiropyrans examined. Kinetic data of the spiro-ring closure for arylazospiropyrans are collected in Table 3.

Non-nucleophilic base. When solutions of MCH_{trans+} were treated with tri-n-butylamine (TBA, 2.0×10^{-3} mol/L), the corresponding open-chain colored merocyanine, MC, is formed immediately. The fast ring-closure reaction that regenerates the original colorless SP was then followed.

When a nucleophilic base such as methoxide ion was used for the deprotonation of MCH_{trans+}, the colored MC was formed immediately and later gave rise to an unknown product, instead of forming the ring-closed spiropyran, SP. The unknown species is presumably a nucleophilic adduct of spiropyrans, formed *via* pseudobase formation on C-2 carbon center or Michael addition to the carbon of the -C–N=- bond of indoline moiety, as shown in Scheme 4. Non-nucleophilic bases such as TBA, triethylamine or tert-butoxide did not show this phenomenum.



Scheme 4

Table 4. Half life times ($t_{1/2}$, sec.) for the ring-closure reaction of 6'-substituted 1,3,3-trimethylindolinobenzospiropyrans

Activated Vs. Non-activated	Substituent	$t_{1/2}$ (sec.) In DMF	$t_{1/2}$ (sec.) In Acetone	Note
Activated	6-NO_2	2.43×10^2	9.49×10	Ref. 11
	6-NO_2, 8-OMe		8.85×10	Ref. 11
	6-NO_2, 8-Br		1.28×10^3	Ref. 11
	6-NO_2, 8-Cl		1.85×10^3	Ref. 11
Borderlined	6,8-dibromo		2.19×10	Ref. 11
	6,8-dichloro		2.42×10	Ref. 11
	6,8-diiodo		1.55×10	Ref. 11
Non-activated	**1**	0.300		This work
	2	2.40		This work
	3	3.20		This work
	4	14.0		This work

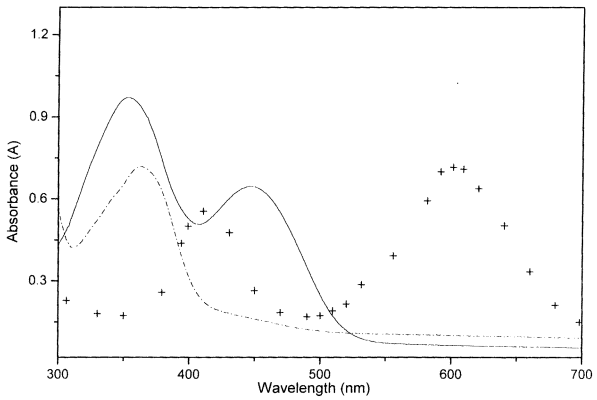


Figure 4. UV-Vis. spectra of various forms of non-activated SP **2** in ethanol. (dotted line: SPH$^+$, solid line: MCH$^+$ and cross-marked point: MC).

UV-Visible absorption spectral data. UV-Visible absorption spectral data of the opened MC form of **1-4** have been obtained in ethanol at 25 °C. All data points in each UV-Vis spectrum are measured in every 10 nm by the stopped-flow spectrophotometry. The opened MC form of non-activated arylazospiropyrans showed their maximum wavelengths at 582-605 nm in ethanol, whereas their conjugated acid form (MCH^+) showed at both 359-363 and 446-461 nm. For an example, UV-Vis. spectra of SP **2** in ethanol are shown in Figure 4. UV-Vis. spectral data of these species are collected in Table 4.

Conclusion

The rate of spiro-ring formation from the opened form of nonactivated spiropyran derivatives, 6-arylazo-1',3',3'-trimethylspiroindolinobenzospiropyrans, **1-4** at room temperature has been determined utilizing the method reported earlier by us. Half life times of the ring-closure reaction in ethanol at room temperature are about 0.3-14 seconds for the non-activated spiropyrans examined.

UV-Visible absorption spectral data of the opened MC form of **1-4** were also obtained utilizing the stopped-flow

Table 5. UV-Visible absorption spectral data (λ_{max}, nm and $\varepsilon \times 10^3$) of non-activated arylazospiropyrans, **1-4** in EtOH

	SP	SPH$^+$	MCH$^+$	MC[a]
1	441 (10.08)	444(9.665)	369 (11.59)	600
			461 (15.79)	
2	287 (19.03)	286 (16.38)	353 (27.76)	605
	361 (21.28)	360 (22.78)	447 (19.03)	
3	290 (14.46)	292 (11.50)	359 (27.98)	602
	370 (1.463)	366 (16.35)	447 (19.10)	
4	280 (28.05)	280 (16.99)	359 (41.12)	582
	371 (16.66)	403 (16.32)	446 (27.51)	

[a]data obtained from stopped-flow method

spectrophotometry. The measured wavelength maxima of those spiropyran dyes are 600, 605, 602 and 582 nm for **1-4** in ethanol, respectively.

Acknowledgment. We acknowledge financial support for this research from the Korea Research Foundation made in the Program Year 1996 (S.R.K) in part and Korean Science and Engineering Foundation (961-0302-2) (S.R.K.).

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