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Synthesis and Photochemical Properties of Novel Spirobenzoselenazolinobenzopyrans

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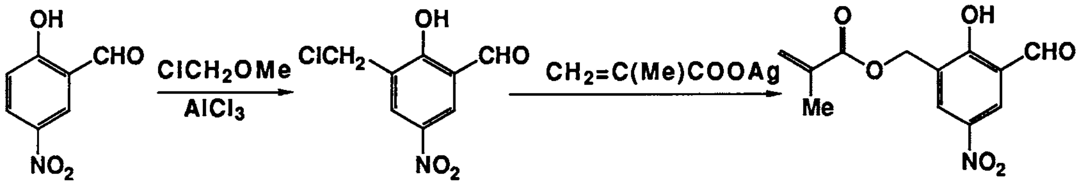
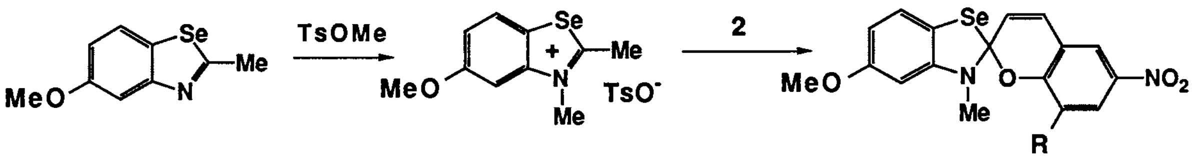
5-Methoxy-3-methyl-6'-nitrospirobenzoselenazolinobenzopyrans have been newly prepared and their reversible structure changes induced by light were characterized by spectroscopic studies. Their stable colored-forms were identified as 5-methoxy-3-methylbenzoselenazolenium-2-*trans*-(5'-nitrostyryl-2'-oxide) being the zwitterionic structure.

Much attention has been currently focused on photochromic spiropyrans for their reversible skeletal isomerization. Although a large number of spiropyrans and their related compounds are synthesized,[1] spectroscopic characterization regarding their structural change in solution due to photochromism remains still unexplored.[2] In this paper, we report synthesis of novel spiropyrans having selenium atom in their framework, and describe their structural assignment related to reversible change induced by light between the colored and colorless forms.

Spirobenzoselenazolinobenzopyrans **1a**-**b** were prepared starting from 5-methoxy-2-methylbenzoselenazole as shown in the equation. The compounds **3** was quantitatively given by the treatment of 5-methoxy-2-methylbenzoselenazole with methyl p-toluene sulfonate (TsOMe) in chloroform at 80 °C in a flame sealed ampoule. 5-Methoxy-3-methyl-6'-nitrospiro[(2'*H*)-1'-benzopyran-2',2-benzoselenazoline] **1a** and 8'-substituted derivative **1b** were cleanly synthesized as deep purple solid by condensation of **3** with 5-nitro-



2b



3

1

R= H, **1a**
$CH_2OCOC(Me)=CH_2$, **1b**

salicylaldehyde derivatives **2**,[3] of which **2b** was quantitatively obtained by chloromethylation and then followed by the treatment with silver methacrylate, in refluxing methanol in the presence of piperidine (**1a**, 35% yield; **1b**, 64%). These spirobenzoselenazolinobenzopyrans **1** were fully characterized by ^{1}H NMR, IR, and MS spectra.[4]

These compounds **1** immediately colored to deep blue or purple by dissolving in chloroform or DMSO respectively, while these colored solutions rapidly bleached by irradiation with visible light (>500 nm) as shown in Fig. 1. The bleached solutions were completely recovered to the original color by being heated at 50 °C. Absorption maxima (λ_{max}) of the colored form which were in the range of 550-560 nm in DMSO were obviously affected by the solvent polarity: those of **1a** and **b** in methanol being shifted to shorter wavelength by 40 nm, but in chloroform toward longer wavelength by 35 nm. This solvent effect on λ_{max} was consistent with the zwitterionic merocyanine structure of the colored form **4** (*vide infra*).[3]

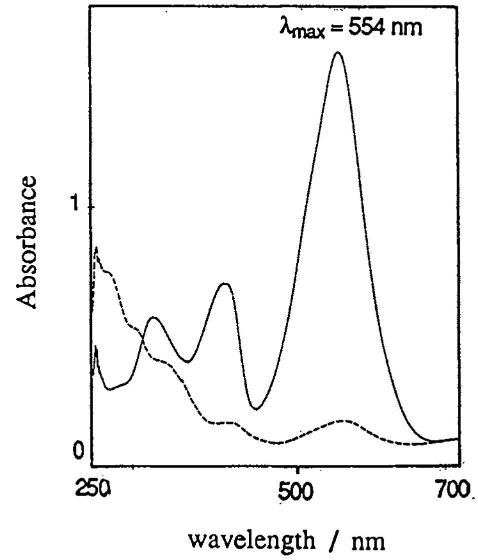
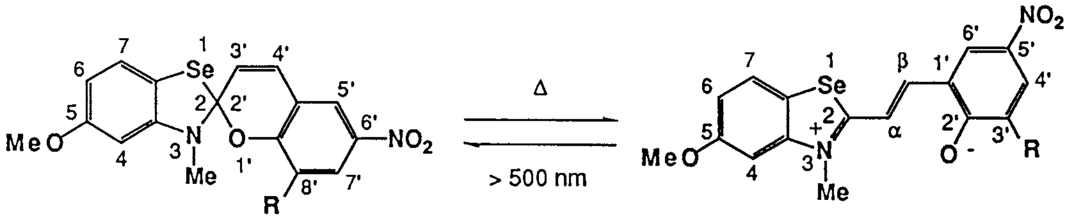


Fig. 1. Absorption spectra of **4b** in DMSO solution. solid line : before irradiation, dashed line : right after irradiation of **4b** with Vis light (>500 nm).

These photobleaching and thermocoloration due to the *negative photochromism*[5] of **1** were investigated in detail to determine the structure related to the colored and colorless forms of **1** on the basis of ^{1}H NMR and ^{1}H-^{1}H COSY experiments.[4] As shown in Fig. 2 (a), the purple solution of **4b** in DMSO-d_6 gave a singlet at 4.06 ppm which was assignable to the quaternary N$^+$-CH_3 group.[3] The vicinal olefinic protons attached to C_α and C_β showed typical trans-coupling ($J_{vic.\ H\text{-}H}$ = 14.4 Hz) which was also proven by homo-nuclear decoupling technique. These spectral data are fully consistent with 5-methoxy-3-methylbenzoselenazolenium-2-*trans*-(3'-methacryloxymethyl-5'-nitrostyryl-2'-oxide) (**4b**) of the merocyanine structure, although further detailed studies on its conformation remains to be explored.[6]

Figure 2 (b) showed ^{1}H NMR spectrum which was taken immediately after irradiation of the purple solution of **4b** with Vis light. Apparently, the new signals appeared could be unambiguously assigned to the colorless spiro-form **1b**[4] by comparison with those of spirobenzothiopyranes,[3] and the peak intensity due to the merocyanine **4b** relatively decreased. The single signal appeared at 3.01 ppm can be assigned to tertiary N-CH_3 group of the colorless spiro-form **1b**.[3]



1 **4**

The signals due to the spiro-form **1b** have gradually decreased at room temperature, and almost disappeared after 2 h. At equilibrium reached in the dark, the signals remained are largely due to the merocyanine **4b**.

On the other hand, ^{1}H NMR spectrum of the purple solutions of **4a** in DMSO-d_6 afforded the characteristic signals assignable both to **1** and **4** after reaching equilibrium in the dark. By heating the equilibrium mixture of **1a** and **4a** in DMSO to 60 °C for 15 min, the solution largely increased its absorption coefficient at 550 nm in electronic spectra. Their population ratios of **4** to **1** at certain temperature could be thus calculated on the basis of the integration of ^{1}H NMR signals of the aromatic protons or the N-CH_3 signal (*vide ante*) which were individually assignable to **1** and **4**.

In Table 1, their ratios (K=[4]/[1]) in DMSO solution together with absorption maxima (λ_{max}), half-lives of the metastable colorless forms **1** ($\tau_{1/2}$), and extinction coefficients (ε) are tabulated. Extinction coefficients (ε) of **4** are thought to be among the largest values of spiropyran derivatives reported.1) Interestingly, substitution at 8'-position (R) significantly affected on $\tau_{1/2}$ and K. Spirobenzoselenazolinobenzopyran having a methacryloxymethyl group **1b** shifted its equilibrium far to the colored form and

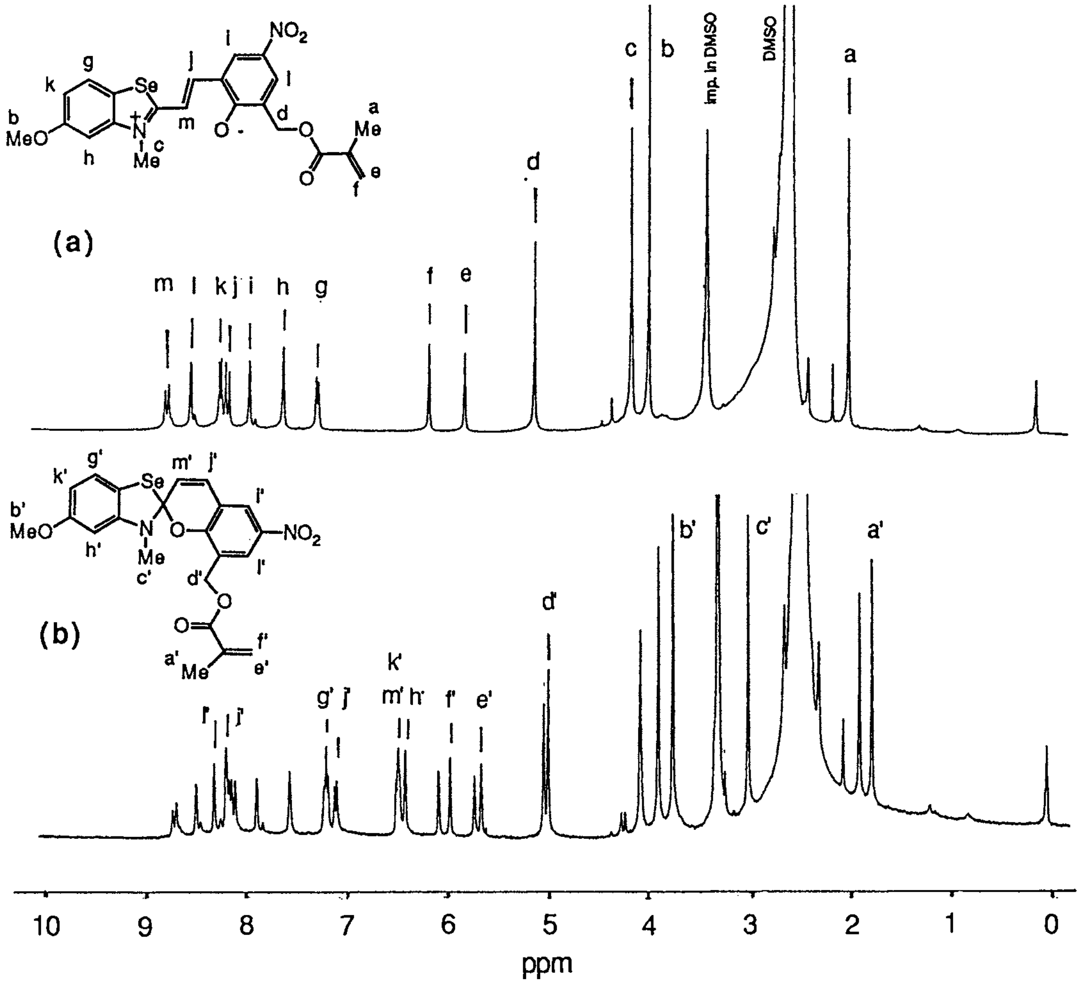


Fig.2. The ^{1}H NMR spectra of **4b** (400 MHz, DMSO-d_6); (a) before Vis light irradiation, (b) right after exposure to Vis light.4)

Table 1. Photochromic properties and selected ^{1}H NMR data of spirobenzoselenazolinobenzopyrans **4** in DMSO at 22 ± 2 °C

	λ_{max}	$\tau_{1/2}$	$\varepsilon \times 10^{-4}$	K	N$^+$-Me	$^3J_{H\alpha\text{-}H\beta}$
	nm	min	mol^{-1}dm^{3}cm^{-1}	([4] / [1])	ppm	Hz
4a	550	80	7.5	0.67	4.23	15.5
4b	554	29	7.3	12	4.06	14.4

gave shorter life-time of the metastable colorless form ($\tau_{1/2}$) than **1a**. This could be accounted for by the steric hindrance around the spiro carbon which must weaken the covalent bond between 1'- oxygen and 2'-carbon of the colorless form. Further detailed investigation on photochromic properties of spirobenzoselenazolinobenzopyrans **1** are now in progress.

References

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2) M. Inouye, M. Ueno, and T. Kitao, *J. Am. Chem. Soc.*, **112**, 8977 (1990).
3) M. Hirano, A. Miyashita, and H. Nohira, *Chem. Lett.*, **1991**, 209.
4) Spectroscopic data for the colorless form **1b** were typically given as follows: IR (cm^{-1}, KBr) 1711 (s, $\nu_{C=O}$), 1590 (s, ν_{C-O}), 1551 (s, $\nu_{asym.\ NO_2}$), 1282 (vs, $\nu_{s.\ NO_2}$); MS (EI, 20 eV) m/z = 487 (M$^+$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.79 (s, C=C-CH_3, 3H), 3.01 (s, N-CH_3, 3H), 3.76 (s, 5-OCH_3, 3H), 4.98 (s, 8'-CH_2, 2H), 5.64 (s, CH_2=C, 1H), 5.94 (s, CH_2=C, 1H), 6.39 (s, 4-C*H*, 1H), 6.46 (m, 3'-C*H* and 6-C*H*, 2H), 7.08 (d, 4'-C*H*, J = 9.6 Hz, 1H), 7.18 (m, 7-C*H*, 1H), 8.16 (s, 5'-C*H*, 1H), 8.28 (s,7'-C*H*, 1H); mp 196-202 °C: the colored form **4b**; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.92 (s, C=C-CH_3, 3H), 3.89 (s, 5-OCH_3, 3H), 4.06 (s, N$^+$-CH_3, 3H), 5.02 (s, 3'-CH_2, 2H), 5.71 (s, CH_2=C, 1H), 6.06 (s, CH_2=C, 1H), 7.17 (d, 7-C*H*, J = 7.8 Hz, 1H), 7.50 (s, 4-C*H*, 1H), 8.06 (d, β-C*H*, J = 14.4 Hz, 1H), 8.13 (d, 6-C*H*, J = 8.0 Hz, 1H), 8.42 (s, 6'-C*H*, 1H), 8.66 (d, α-C*H*, J = 14.4 Hz, 1H). The olefinic protons of **4b** (α-C*H* and β-C*H*) were determined by comparison of its NMR spectrum with that of the merocyanine of 3,3-dimethylspirobenzopyrane derivative.$^{2)}$
5) A few spiropyrans, especially those bearing hydroxy, carboxy, or amino groups on either ring, are reported to exhibit negative photochromism because of the stabilization due to intramolecular hydrogen-bond in the merocyanine structure. See, E. Inoue, H. Kokado, I. Shimizu, H. Kobayashi, and Y. Takahashi, *Bull. Chem. Soc. Jpn.*, **45**, 1951 (1972); *ibid.*, **42**, 1730 (1969); J. Sunamoto, K. Iwamoto, M. Akutagawa, M. Nagase, and H. Kondo, *J. Am. Chem. Soc.*, **104**, 4904 (1982).
6) NOE experiments to determine the conformation of **4** were carried out. Irradiation of 6'-C*H* resulted in significant changes in the intensities of β-C*H* (+10%) and α-C*H* (-12%), while irradiation of N$^+$-CH_3 gave no apparent NOE for α-C*H* or β-C*H*. Consequently, the alternative structure (s-cis, s-cis) for **4** cannot be ruled out.

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