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Metastable Solution Structures of Spirobenzoselenazolinobenzopyrans and Their Negative Photochromic Properties

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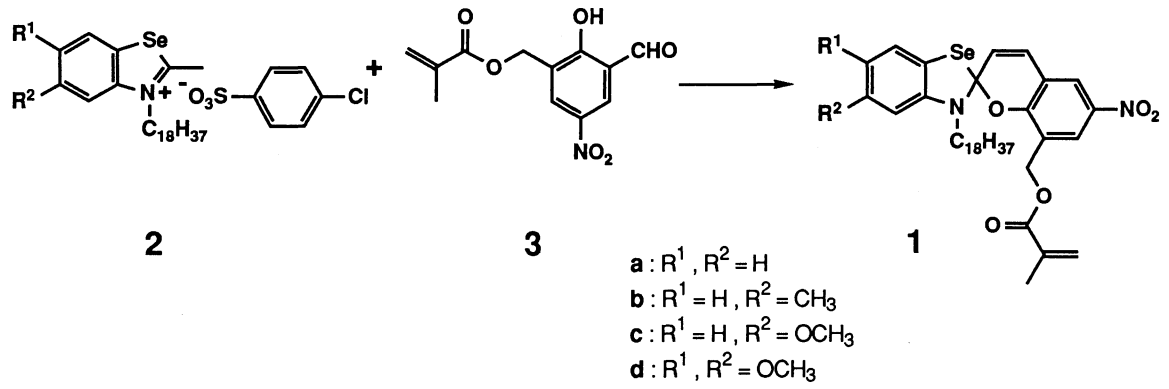
A series of photochromic 6'-nitro-3-octadecylspirobenzoselenazolinobenzopyrans have been newly prepared and their solution structures of the colored form have been confirmed as 3-octadecylbenzoselenazolenium-2-*trans*-1'-*cis*-(5'-nitrostyryl-2'-oxide) by selective partial deuteration and NMR techniques. Photochromic repetition of these compounds for 50 % fatigue attained the number more than ca. 800 times.

In recent years, various organic photochromic compounds have been extensively studied because of potential applicability to photo-information memory devices. Although a number of spiropyran derivatives have been prepared,[1] detailed studies on their structural transformation were still remain unexplored.[2]

Previously, we reported the first synthesis of spirobenzoselenazolinobenzopyrans and their photochemical properties,[3] while their solution structures could not be confirmed because of two possible isomers. In this paper, we report here preparation and detailed solution structure of spirobenzoselenazolinobenzopyran, and describe their substituent effect on the photochemical properties and solvent effect on photochromic repetition durability between photo-bleaching and coloration.

A series of spirobenzoselenazolinobenzopyrans **1a-d** were prepared by the synthetic method described previously except using *p*-chlorobenzenesulfonic acid salts **2** for alkylating reagents to obtain **1** with much better yields.[3,4] These products obtained were purified by silica gel column chromatography in the dark and were fully characterized by IR, ^{1}H-NMR, and MS spectra and elemental analysis.[5]



2 **3** **1**

a : R^1 , R^2 = H
b : R^1 = H , R^2 = CH_3
c : R^1 = H , R^2 = OCH_3
d : R^1 , R^2 = OCH_3

All these compounds **1** showed negative photochromism in various solvents. That is, these compounds **1** immediately colored to purple or reddish purple by dissolving in chloroform or DMSO, while these colored solutions rapidly bleached by irradiation with Vis light (>500 nm). Figure 1 shows that these bleached solutions

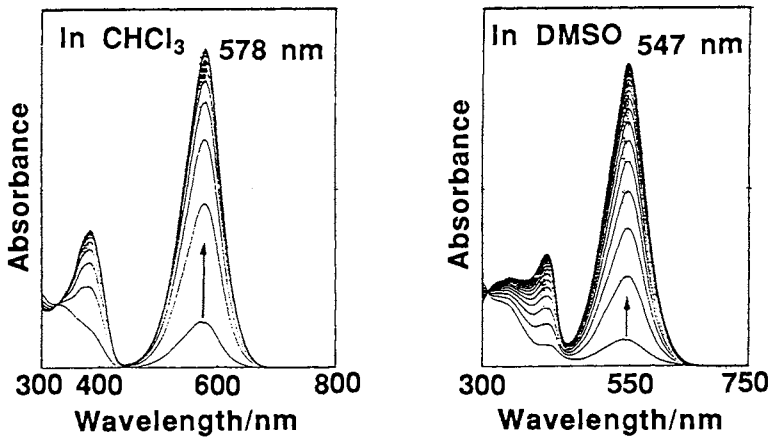


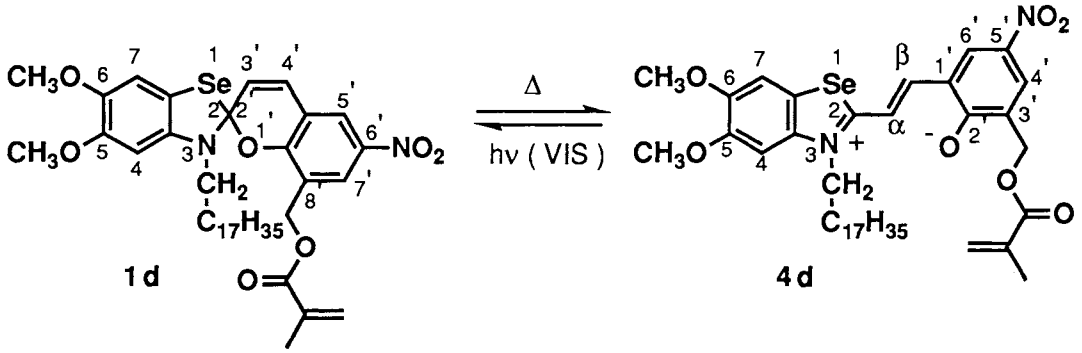
Fig. 1. UV-Vis spectral changes of the colorless solutions of **1a.** Each spectrum was recorded at 90-second intervals immediately after irradiating a purple solution of **4a** by Vis light.

Table 1. Photochromic properties of spirobenzoselenazolinobenzopyrans

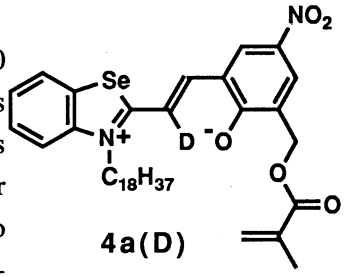
	In $CHCl_3$			In DMSO		
	λ_{max} / nm	$\varepsilon x10^{-4}$ / $M^{-1}cm^{-1}$	$\tau_{1/2}$ [a] / min	λ_{max} / nm	$\varepsilon x10^{-4}$ / $M^{-1}cm^{-1}$	$\tau_{1/2}$ [a] / min
1a	578	5.0	2.0	547	4.3	4.0
1b	580	4.9	1.9	550	4.1	4.8
1c	586	4.6	2.5	557	3.8	4.3
1d	583	5.5	2.6	555	4.7	5.6

a) Half life of the metastable colorless spiro-form of **1** at 25 °C.

of **1a** thermally returned to the colored state. Absorption maxima (λ_{max}), molar extinction coefficient (ε), and half life of the metastable colorless form ($\tau_{1/2}$) were tabulated in Table 1. These blue shifts of λ_{max} in a polar solvent such as DMSO may be ascribed to their colored forms of a zwitterionic structure. This may be compatible with its chemical shift of N-CH_2- in ^{1}H-NMR. Namely, the CH_2 group bonded to the quaternary N^+ of **4d** appeared at 4.41 ppm in $CDCl_3$, while that of **1d** showed triplet at 3.55 ppm.[3]



The determination of olefinic protons of **4** (H_α and H_β) was made by comparison of NMR spectra of **4a** with **4a(D)** which was prepared from the corresponding deuterated precursor **2a(D)** derived by heating of **2a** in CH_3OD.[6]



^{1}H-NMR spectra of the metastable colorless form **1d** were measured at -40 °C immediately after irradiating a purple solution of **4d** by Vis light (>500 nm) as shown in Fig. 2. Each peak in ^{1}H-NMR spectra of the ring-opened form **4** was fully assigned in conjunction with ^{1}H^{1}H-COSY. Furthermore, ^{1}H-NMR nuclear overhauser effect (NOE) difference experiments were substantially consistent to the (*s-trans*, s-*cis*) structure of 3-octadecylbenzoselenazolenium-2-*trans*-1'-*cis*-(5'-nitrostyryl-2'-oxide) (**4d**). That is, irradiation on the N-CH_2- caused positive NOE on the absorption due to H-4 aromatic hydrogen and H_α olefinic one (8% and 6%, respectively). Additionally, irradiation of the H_β gave rise to 8% enhancement of the signal intensity due to H-6' aromatic hydrogen.

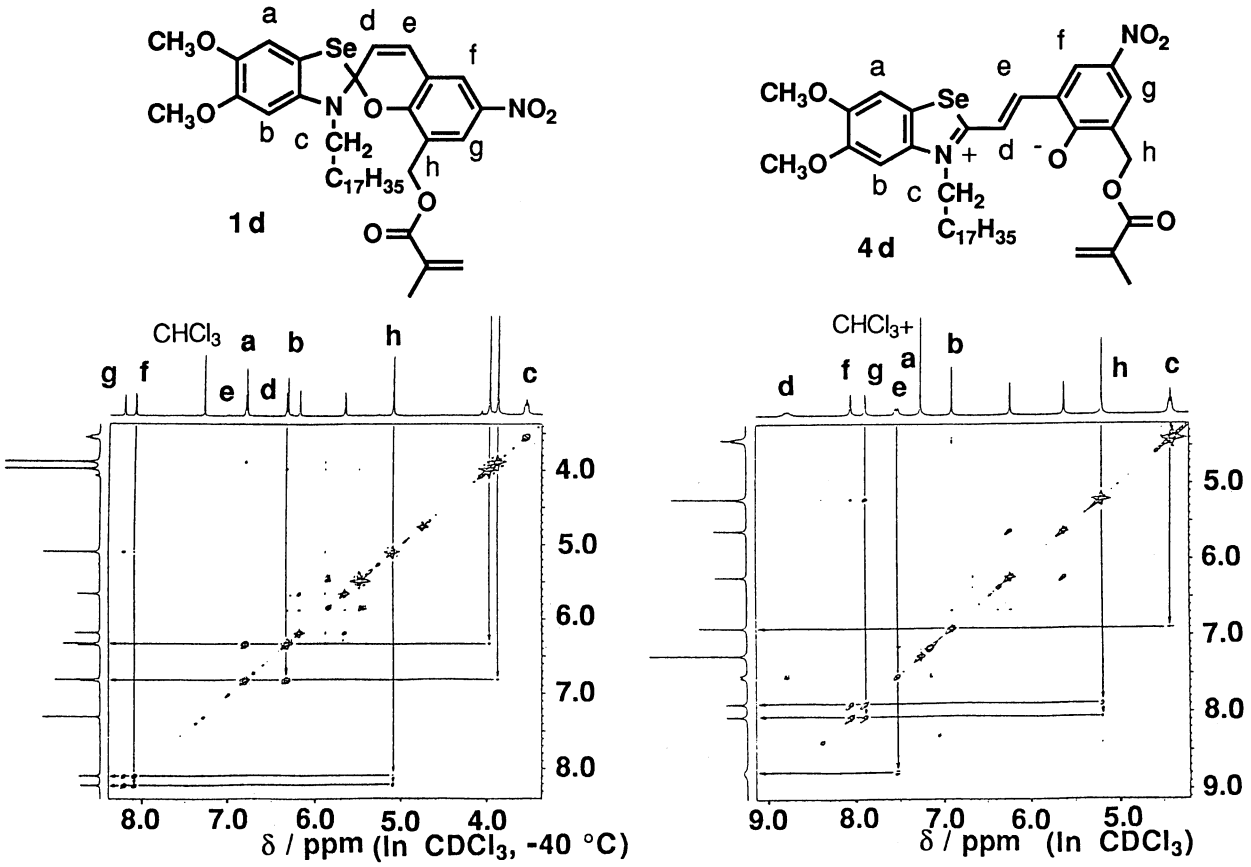


Fig. 2. ^{1}H^{1}H-COSY spectra of sample **1d** and **4d**.

One of the interesting features of these compounds **1** is repetitive durability between photo-bleaching and thermo-coloration. This photochromic property was affected remarkably by a kind of solvent. Figure 3 demonstrates photochromic repetition of **1a** in DMSO attained the number more than ca. 800 times until the apparent absorbance at λ_{max} reached into 50% of the initial absorbance, while that in $CHCl_3$ fell off to 40 times.

In mass spectral analysis of the fatigued compounds of **1a** in $CHCl_3$ obtained after repetitive irradiation of Vis light (>500 nm) for bleaching and heating for coloration under N_2, it was detected several halogenic adducts of **1a** such as **1a**+Cl, **1a**+2Cl, **1a**+CCl_3 etc. Certain halogenic species generated from $CHCl_3$ may apparently accelerate fatigue of their photochromic properties. Further detailed studies on photochemical properties of these related compounds are now in progress.

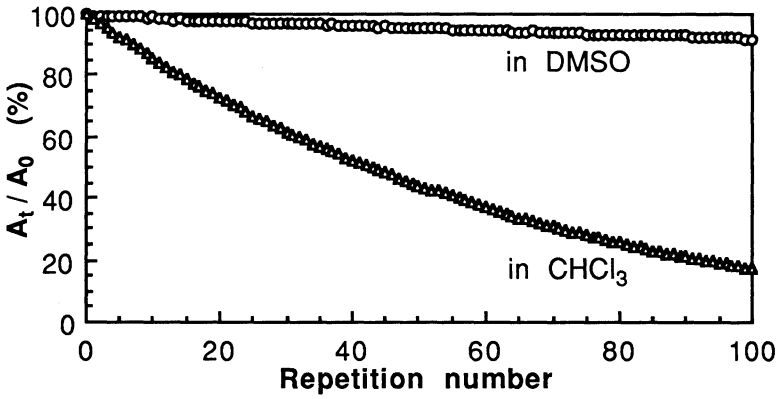


Fig. 3. Photochromic repetition of **1a** on photon-thermal mode. Repetition of Vis light (>500 nm) irradiation for 10 second and heating at 50 °C for 3 min.

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5) Spectroscopic data for the colorless form **1d** were typically given as follows : ^{1}H-NMR (400 MHz, $CDCl_3$, -40 °C) δ 0.87 (t, C*H*$_3$, 3H), 1.23 (m, -(C*H*$_2$)$_{15}$-, 30H), 1.76 (m, N-CH$_2$-C*H*$_2$-, 2H), 1.96 (s, C=C-C*H*$_3$, 3H), 3.55 (t, N-C*H*$_2$-, 2H), 3.87 (s, OC*H*$_3$,3H), 3.97 (s, OC*H*$_3$, 3H), 5.09 (s, 8'C*H*$_2$, 2H), 5.66 (s, C*H*$_2$=C, 1H), 6.18 (s, C*H*$_2$=C, 1H), 6.32 (s, 4C*H*, 1H), 6.33 (d, 3'=C*H*, 1H, *J*=9.5 Hz), 6.81 (s, 7C*H*, 1H), 6.82 (d, 4'=C*H*, 1H, *J*=9.7 Hz), 8.08 (d, 5'C*H*, 1H), 8.21 (d, 7'C*H*, 1H) : the colored form **4d** : IR (cm^{-1}, KBr) 1718 (s, νC=O), 1555 (s, ν_{as} NO_2), 1298 (vs, ν_s NO_2), 1230 (s, ν_{as} C-O-C), 1030 (s, ν_s C-O-C). MS (EI, 20 eV) m/z=756 (M+). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 0.87 (t, C*H*$_3$, 3H), 1.23 (m, -(C*H*$_2$)$_{15}$-, 30H), 1.92 (qui, N-CH$_2$-C*H*$_2$-, 2H), 2.03 (s, C=C-C*H*$_3$, 3H), 3.99 (s, OC*H*$_3$, 3H), 4.00 (s, OC*H*$_3$, 3H), 4.41 (t, N-C*H*$_2$-, 2H), 5.19 (s, 3'C*H*$_2$, 2H), 5.62 (t, C*H*$_2$=C, 1H), 6.23 (s, C*H*$_2$=C, 1H), 6.89 (s, 4C*H*, 1H), 7.26 (s, 7C*H*, 1H), 7.52 (d, =C*H*$_\beta$, 1H, *J*=13.8 Hz), 7.86 (d, 4'C*H*, 1H), 8.03 (d, 6'C*H*, 1H), 8.77 (br.d, =C*H*$_\alpha$, 1H, *J*=ca.13 Hz). Elemental Analysis. Found: C, 63.42; H, 7.54; N, 3.84%. Calcd: C, 63.56; H, 7.47; N, 3.71%.

6) D% of **4a(D)** determined by ^{1}H-NMR was ca. 60%.

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