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Photochromic Properties of a New Spirobenzothiopyran Compound

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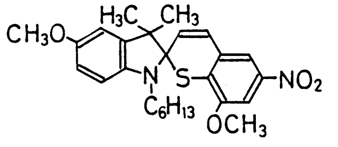
Photochromic processes of 1′-hexyl-5′,8-dimethoxy-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzothiopyran-2,2′-indoline] were investigated with laser flash techniques. Photocoloration was found to proceed via the excited singlet state, and the quantum yield of coloration was an order of magnitude smaller than those of ordinary spirobenzopyrans. The main route of the decoloration was found to be the thermal reaction. Remarkably different solvent effects for the thermal fading rate of the colored form were observed, which indicates that the zwitterionic structure is more significant for the new spirobenzothiopyran than ordinary spirobenzopyrans. Repetitive cycles of photocoloration and thermal fading were achieved.

Photochromism of spirobenzothiopyran was first reported by Becker and Kolc.1) They synthesized 1′,3′,3′-trimethylspiro[2*H*-1-benzothiopyran-2,2′-indoline], and observed its colored form at 77 K. The colored form was thermally unstable, and bleached at elevated temperatures. The photochemical processes of coloration and decoloration have not as yet been investigated.

Recently, a new series of spirobenzothiopyrans was synthesized.2) The thermal stability of the colored forms observed at room temperature upon irradiation with UV light of these new compounds was improved by introducing a nitro group in the benzothiopyran ring. The absorption spectra of the colored forms in a polymer matrix are reported to extend to wavelengths as long as 900 nm, and application as optical recording media for laser is expected.

In the present work, the photochromic reactions of a typical compound of the new spirobenzothiopyrans, 1′-hexyl-5′,8-dimethoxy-3,3′-dimethyl-6-nitrospiro-[2*H*-1-benzothiopyran-2,2′-indoline] (Scheme 1), were investigated with laser flash techniques. The solvent effect on the fading rate and the absorption spectrum was also studied in order to assign the structure of the colored form.



Scheme 1.

Results and Discussion

Coloration and Decolortation Processes. The absorption spectrum of the colorless form is independent of the kind of solvent, and has maxima at 310 nm and 400 nm. Fluorescence was not detected at room temperature, which is in agreement with the result of Becker and Kolc.1) Although they attempted to observe emission at 77 K, no emission characteristics of 1′,3′,3′-trimethylspiro[2*H*-1-benzothiopyran-2,2′-indoline] was detected.

The photocoloration process was investigated in aerated and degassed solutions of ethanol (EtOH) and *N,N*-dimethylformamide (DMF). The colorless form was excited at 360 nm. Figure 1 shows the transient absorption spectra in aerated and degassed EtOH solutions, measured immediately after the laser pulse. There is no significant difference between the two spectra. The shape of the spectrum was that of the colored form, and no reaction intermediates were detected. Similar results were obtained in aerated and degassed DMF solutions.

Kinetic measurements of the coloration process were made at the wavelength of the absorption maximum of the colored form (620 nm in EtOH, 660 nm in DMF). The absorbance of the colored form was proportional to the laser energy, indicating a single photon process. Figure 2 shows the result of the kinetic measurements of the coloration process in EtOH solution. The time that the absorption change lags behind the time-integrated laser intensity is very small. We assumed a linear response of the reaction to the laser pulse, and obtained a good fit of the experimental results with the calculated absorption changes using various rate constants. The coloration proceeds by first-order kinetics, and the colorlation rates were determined to be 7×10^{7} s^{-1} in EtOH and 8×10^{7} s^{-1} in DMF. No significant

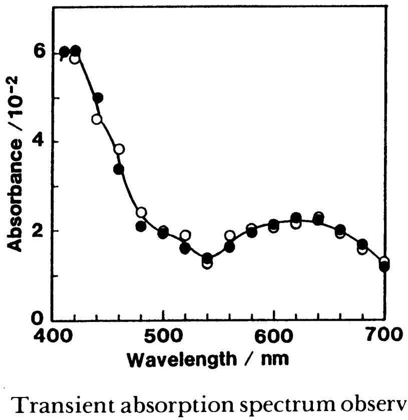


Fig. 1. Transient absorption spectrum observed 30 ns after a laser pulse in aerated(○) and degassed(●) EtOH solutions.

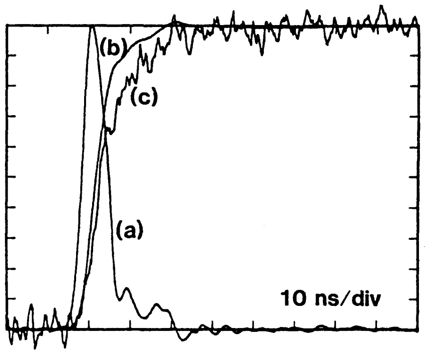


Fig. 2. The photocoloration process in ethanol solution. The laser profile(a), its time-integrated intensity(b), and the absorption change of the colored form(c) are shown. Each curve is normalized to unity.

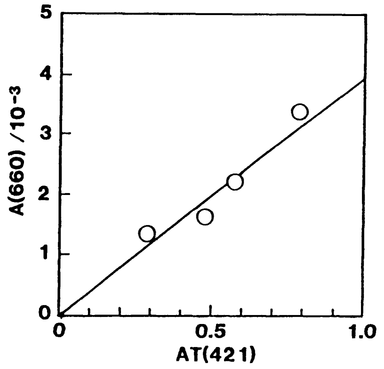


Fig. 3. The plot of the absorption of the colored form in degassed DMF, $A(660)$ vs. the triplet–triplet absorption of anthracene, $AT(421)$.

difference was found in the observed rate constants for degassed and aerated solutions, or for aprotic and protic solvents.

In order to determine the reaction state of the coloration process, we performed triplet quenching experiments on the photoexcited colorless form in degassed EtOH solution using ferrocene (triplet energy 159 $\mathrm{kJ\,mol^{-1}}$ [3]) as a quencher. It is reasonable to assume that the triplet energy level of the colorless form is much higher than that of ferrocene, so the triplet-triplet energy transfer from the colorless spirobenzothiopyran to ferrocene may proceed with the diffusion-controlled rate constant, k_d ($=9.2\times10^9\ \mathrm{s^{-1}}$ [4]). The observed rate of the coloration, k, is given by $k=k_0+k_d$ [Ferr], where k_0 is the coloration rate constant in the absence of ferrocene. However, even when ferrocene was added up to a concentration of $1\times10^{-1}\ \mathrm{mol\,dm^{-3}}$, the observed rate of the coloration was not changed. These results indicate that the coloration does not proceed via the triplet state of the uncolored form. Therefore, the reaction state must be the excited singlet state.

Quantum yields of the coloration reaction were determined in degassed solutions of EtOH and DMF by using the triplet-triplet absorption of anthracene in degassed EtOH solution as a relative standard as described in Ref. 5. Figure 3 shows the relationship between the absorption of the colored form at 660 nm, $A(660)$, in degassed DMF and the triplet-triplet absorption of anthracene at 421 nm, $AT(421)$. The quantum yield is estimated from the slope of the plot, and is 4.8×10^{-2} in EtOH and 1.8×10^{-2} in DMF. These values are an order of magnitude smaller than those of the ordinary spirobenzopyrans,[6] which indicates that the deactivation process due to the sulfur atom is efficient for the new spiro compound.

We also carried out laser flash experiments on the decoloration reaction, in which the colored form was excited in the wavelength region on the longer wavelength side of the absorption spectrum. In aerated solutions, decoloration was observed, while, in degassed solutions, no decoloration of the colored form was observed under these experimental conditions. Therefore, the photodecoloration observed in aerated solution was due to photooxidation, and the conversion of the colored form to the colorless form mainly occurs by way of a thermal reaction in the ground state.

Solvent Effect. The thermal stability of the colored form is affected by the solvent polarity. A number of studies have been made for the ordinary spirobenzopyrans, and the colored forms are best regarded as zwitterionic species.[7] The logarithm of the fading rate constant decreases linearly with increasing Kosower's Z or Brownstein's S values. However, the plot against the $(D-1)/(D+2)$ gives a nonlinear graph, and is different for protic and aprotic solvents, where D is the dielectric constant of the solvent. These results can be interpreted in terms of the hydrogen bonding between the colored form and protic solvents.[7]

For the new spirobenzothiopyran, the thermal fading rate, k_T, at 25 °C and the wavenumber of the absorption maximum of the colored form, $\tilde{\nu}_{max}$ was measured in methanol (MeOH), ethanol (EtOH), isobutyl alcohol (*i*-BuOH), tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), and summarized in Table 1. Remarkably different solvent effects for the thermal fading rate were observed for this compound. Figure 4 shows the plot of the logarithm of k_T against Dimroth's E_T

Table 1. Effects on the Solvent Polarity on the Rate Constant of Thermal Fading, k_T, (25 °C) and the Wavenumber of the Absorption Maximum of the Colored Form, $\tilde{\nu}_{max}$

Solvent	Dielectric constant(D)	E_T / $\mathrm{kJ\,mol^{-1}}$	k_T / $\mathrm{s^{-1}}$	$\tilde{\nu}_{max}$ / $\mathrm{cm^{-1}}$
MeOH	32.6	232	2.8×10^{-4}	1.66×10^{4}
EtOH	24.3	217	6.9×10^{-3}	1.61×10^{4}
i-BuOH	15.2	196	9.4×10^{-3}	1.59×10^{4}
DMSO	48.9	188	4.3×10^{-4}	1.56×10^{4}
DMF	36.7	183	2.8×10^{-3}	1.51×10^{4}
THF	7.93	156	3.1×10^{-1}	1.39×10^{4}

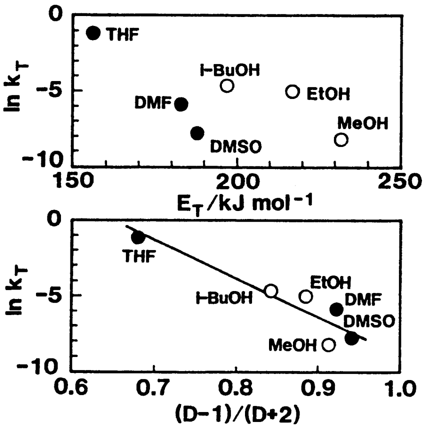
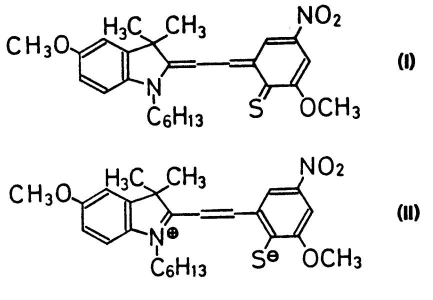


Fig. 4. The plots of ln k_T vs. E_T (upper half) and $(D-1)/(D+2)$ (lower half). The solid circle represents the aprotic solvent, and the open circle protic solvent.

values[8] (E_T is linearly related to the S and Z values) and $(D-1)/(D+2)$. With increasing value of E_T and $(D-1)/(D+2)$, k_T decreases. A linear relationship was obtained against $(D-1)/(D+2)$, rather than against E_T, which is contrary to the ordinary spirobenzopyrans. For the new spirobenzothiopyran, the hydrogen bonding effect on the thermal stability of the colored form in protic solvents as observed in the ordinary spiropyran was not marked.

For the structure of the colored form of the new spirobenzothiopyran, two resonance forms, the thione structure **I** and the zwitterionic structure **II** (Scheme 2) are considered. Becker and Kolc assigned the structure of the colored form of a spirobenzothiopyran to be similar structure to **I**, by comparing the spectral characteristics at 77 K with the colored forms of the chromenes, 2*H*-1-benzothiopyrans, and spiro[benzopyran-2,2′-indolines].[1]

However, the dependence of k_T on the $(D-1)/(D+2)$ value can not be explained in terms of the thione structure **I**. The k_T value for the new spirobenzothiopyran is on the same order (ca. 10^{-4} s^{-1}) as that for the ordinary spirobenzopyran[7] in a highly polar solvent such as MeOH. On the other hand, k_T for the new spirobenzothiopyran in THF is about 10 times larger than that for the ordinary spirobenzopyran, and the colored form of the new spirobenzothiopyran becomes very unstable in a solvent with a small $(D-1)/(D+2)$ value. These results imply that the contribution of the zwitterionic structure is even larger for the new spirobenzothiopyran than for the ordinary spirobenzopyran.



Scheme 2.

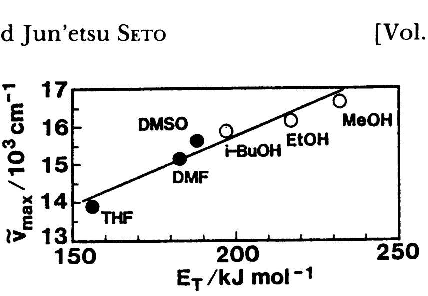


Fig. 5. The plots of $\tilde{\nu}_{max}$ vs. E_T. The solid circle represents the aprotic solvent, and the open circle the protic solvent.

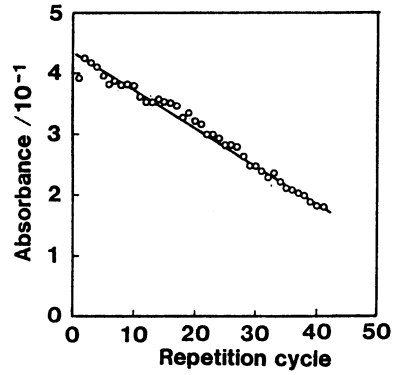


Fig. 6. The absorption decay of the colored form on the repetitive UV coloration and thermal fading cycles.

Figure 5 shows the plots of the wavenumber of the absorption maximum of the colored form, $\tilde{\nu}_{max}$, against the Dimroth's E_T value. $\tilde{\nu}_{max}$ increases with increasing value of E_T, and a hypsochromic effect was observed. A linear plot was obtained against the E_T value. This result indicates that the polarity of the colored form in the excited state is lower than that in the ground state, which can be interpreted in terms of the zwitterionic structure **II**.

Cycle Lifetime and Recording Characteristics. The new spirobenzothiopyran could be repetitively colored and bleached by irradiating with UV and by thermal treatment respectively. We performed repetitive coloration and decoloration in degassed DMF solution containing 10^{-4} mol dm^{-3} of the spirobenzothiopyran. With 2 minutes of UV irradiation, more than 30 cycles were achieved before the absorption of the colored form at the maximum decreased to 50% of the initial value (Fig. 6). The value of the cycle lifetime is on the order of 10 even in a dilute solution, which is promising with regard to practical application.

We examined the recording characteristics of a disk medium with a multilayer structure, in which the new spirobenzothiopyran was used as the sensitive material. The recording was carried out with a laser diode lasing at 780 nm. A carrier-to-noise ratio of more than

54 dB was achieved with a carrier frequency of 1 MHz.[9)]

In conclusion, we first investigated the photochromic processes of a spirobenzothiopyran compound, and found that photocoloration proceeds via the excited singlet state, and the quantum yield of coloration is an order of magnitude smaller than those of ordinary spirobenzopyrans. The main route of the decoloration was found to be the thermal reaction. Remarkably different solvent effects for the thermal fading rate were observed, and the zwitterionic structure was significant for the new spirobenzothiopyran than for ordinary spirobenzopyrans.

Experimental

The spirobenzothiopyran was synthesized as described elsewhere.[1)] All the solvents used methanol (MeOH), ethanol (EtOH), isobutyl alcohol (*i*-BuOH), tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO)) were spectral-grade. Typical concentration of the spiropyran was 1×10^{-4} mol dm^{-3}.

Photochemistry of the coloration and decoloration process was investigated in aerated and degassed solution of EtOH and DMF. Excitation was from a pulsed dye laser (FWHM>8 ns, output>10 mJ) optically pumped by a XeCl excimer laser. The absorption change was detected by a K-367 laser kinetic spectrometer (Applied Photophysics). The photomultiplier signal was recorded on a Tektronix 7912AD programmable digitizer, and analyzed by using a personal computer. Quantum yields of coloration were determined by using the triplet–triplet absorption of anthracene in degassed EtOH solution as a relative standard. The values used were 5.2×10^4 dm^3 mol^{-1} cm^{-1} for the molar extinction coefficient[10)] and 0.7 for the triplet yield.[11)] The molar absorption coefficient of the spiropyran was estimated by the extrapolation of the coloration curves in degassed solutions to be 8.5×10^3 dm^3 mol^{-1} cm^{-1} (620 nm) in EtOH and 8.0×10^3 dm^3 mol^{-1} cm^{-1} (660 nm) in DMF.

The solvent effect on the thermal fading and the absorption spectra in various solvents were monitored with a Hitachi 320 spectrophotometer. A 500 W high pressure mercury lamp with a Toshiba UV-D36 and a IRA-25S glass filters was used for the coloration source for the repetitive coloration and thermal fading experiments.

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