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The Role of Triplet State of Nitrospiropyran in Their Photochromic Reaction

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The effects of intermolecular and intramolecular triplet quenchers and sensitizers on the photochromism of nitrospiropyran have been examined in order to clarify the role of the triplet state (^{3}A*) as well as that of the excited singlet state (^{1}A*). The rates of photocoloration and fatigue were significantly affected: the quenchers retarded both rates, while the sensitizers retarded the former but enhanced the latter rate. It can be concluded that more than 90% of the total amount of photomerocyanin is generated from ^{1}A* in the photostationary state and that fatigue proceeds mainly through ^{3}A*.

Photochromism is now being extensively re-investigated, mainly from the viewpoint of application to EDRAW (erasable and directly reading and writing) memories. In order to reach the goal, there are several routes which must be attacked. One is to develop novel preparative procedures of highly fatigue-resistant, thermally stable photochromic compounds. So far, though, only a few compounds satisfy these demands.[1,2] Another route is to modify popular photochromic compounds so as to improve their photochromic peculiarity. Spiropyran is one of the most well-known photochromic families, and is transformed either photochemically or thermally between a colorless closed spiro-form (SP) and a colored open merocyanin form (PMC).[3] Its analogues become deeply colored by UV irradiation with high sensitivity, but are rather sensitive to fatigue. The elucidation of the photochromic mechanism of this family may be important not only for basic interest, but also practical applications to photochromic memories.

Since the photochromism of spiropyrans was found in the 1950's,[4,5] a large number of papers have appeared concerning their photophysical and photochemical behavior in various matrices.[3] 1′,3′,3′-Trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (**1**) and its derivatives have stimulated special attention since their sensitivity is so high, even in the near-UV region up to 400 nm. Recently, the photophysical and photochemical processes of their photochromism have been elucidated by both picosecond and nanosecond laser photolysis.[6–9] It has become clear that PMC is generated in the nanosecond range, mainly through the excited singlet state of SP. An intriguing argument is whether the triplet state effectively contributes to the photochromic reaction or not. The reaction mechanisms proposed so far are different with respect to the role of the triplet state. The mechanism of the fatigue process still remains ambiguous.

It is known that benzophenone is a good triplet sensitizer of **1**.[10] On the other hand, naphthalene derivatives have triplet energies slightly lower than that of **1**[10] and, therefore, can act as a triplet quencher. Therefore, compounds **2—4**, which have a triplet sensitizer or a quencher intramolecularly linked as a side group, have been prepared in order to evaluate the efficiency of photo-reactions via the triplet states. The aim of this paper is to clarify the various factors which influence the photochromic efficiency and photodurability of **1**.

Results and Discussion

Effects of Triplet Sensitizer and Quencher on the Photocoloration. The dependence of the build-up of PMC on the benzophenone concentration (0, 0.02, and 0.1 M, M=mol dm^{-3}) upon 313-nm light irradiation of **1** in acetonitrile under argon is shown in Fig. 1. Since the triplet energies (E_T) of benzophenone and **1** are 69.2 and 64.3 kcal mol^{-1}, respectively, and the concentration of **1** was high (2.7×10^{-4} M), triplet energy transfer must have occurred with an efficiency of nearly unity. Figure 1 indicates that both the initial rate (slope) and photostationary level of PMC formation (asymptotic value) decrease with increasing concentration of the sensitizer. Similar results were obtained for other sensitizers, such as xanthone (E_T 74.1 kcal mol^{-1}) and *p*-bromoacetophenone (E_T 71.4 kcal mol^{-1}).

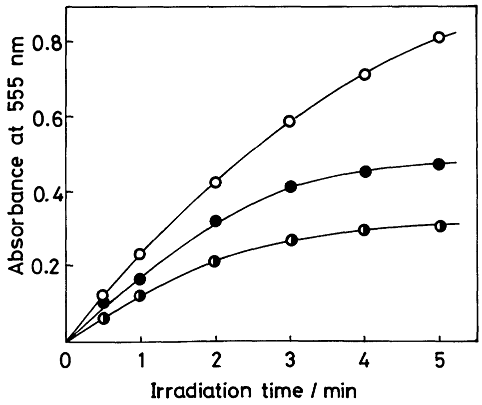


Fig. 1. Dependence of build-up of PMC on benzophenone concentration. [**1**]=2.7×10^{-4} M. ○: [Benzophenone]=0, ●: 0.02 M, and ◑: 0.1 M. Solvent=acetonitrile. Irradiation light: 313 nm.

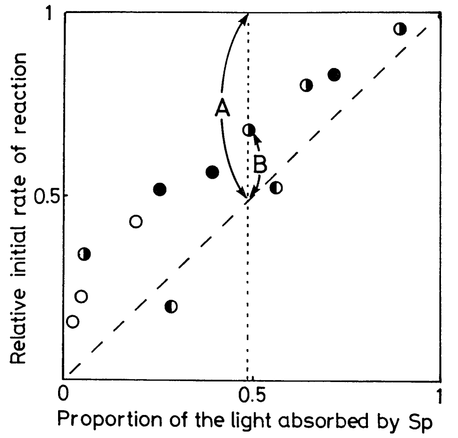


Fig. 2. Initial rate of photocoloration of **1** in the presence of triplet sensitizers or quenchers. ○: Xanthone (E_T=74.1 kcal mol^{-1}), ●: *p*-bromoacetophenone (E_T=71.4 kcal mol^{-1}), ◑: benzophenone (E_T= 69.2 kcal mol^{-1}), and ◐: benzil (E_T=54.3 kcal mol^{-1}). [**1**]=2.7×10^{-4} M. [Sensitizer] or [quencher]=2.7×10^{-3}—5.0×10^{-1} M. Solvent=acetonitrile. Irradiation light: 313 nm.

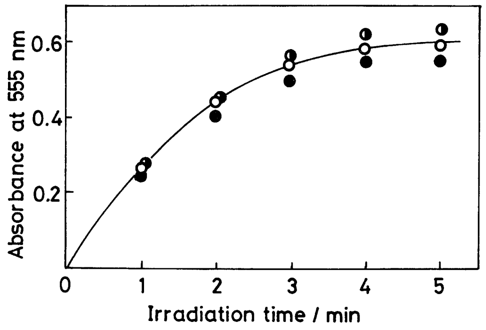


Fig. 3. Dependence of build-up of PMC on 1,1′-binaphthyl concentration. [**1**]=2.7×10^{-4} M. ○: [1,1′-Binaphthyl]=0, ●: 0.004 M, and ◑: 0.015 M. Solvent= acetonitrile. Irradiation light: 313 nm.

During the initial stage of photocoloration, incident light is exclusively absorbed by the sensitizer and SP, the absorption by PMC being negligible. Therefore, the relative amounts of the light quanta absorbed by the sensitizer and SP can be readily estimated from their absorbances at the irradiation wavelength. The initial coloration rates measured in the presence of various sensitizers are plotted against the light quanta absorbed by SP in Fig. 2, where the values of both axes are normalized by the respective values obtained in the absence of a sensitizer. The broken line passing through the origin and a point [1,1] refers to the relative coloration rate induced by the light absorbed by **1**, itself, since the rate is proportional to the absorbed light quanta. In the presence of additives, the apparent coloration rate by direct excitation should be reduced by an amount *A* to the value given on the broken line, owing to a filtering effect of the sensitizer. As plotted in Fig. 2, the rates observed for sensitizers with an E_T higher than that of **1** are located above the broken line. On the other hand, the rates plotted for benzil (E_T 54.3 kcal mol^{-1}), which is a triplet quencher, are located under the broken line.

The rates corresponding to the experimental ones minus those on the broken line (as noted as *B*) are due to triplet sensitization. As shown in Fig. 2, *B* is much less than *A*. Interestingly, the ratio of *B* to *A* was about 1/3 in almost all experimental runs. This means that the coloration rate by triplet sensitization relative to that by direct excitation is ca. 0.3.

Since the light energy absorbed by the sensitizers is transferred with an efficiency of almost unity to generate the triplet state of SP under the present experimental conditions, a relationship can be deduced:

$$\frac{\text{Coloration efficiency of } {}^3\text{SP*}}{\text{Coloration efficiency on direct excitation}} = \frac{1}{3}. \tag{1}$$

The triplet sensitizers are effective for PMC formation, but the efficiency is not so high; they serve, rather, as an internal filter. As described above, benzil, the E_T value of which is lower than that of SP **1**, served as a quencher of PMC formation. 1,1′-Binaphthyl (E_T 60 kcal mol^{-1}) also has a lower E_T value than **1**; however, its quenching efficiency was very low, as shown in Fig. 3. These results indicate that the singlet state of SP plays an important role in its coloration upon direct irradiation.

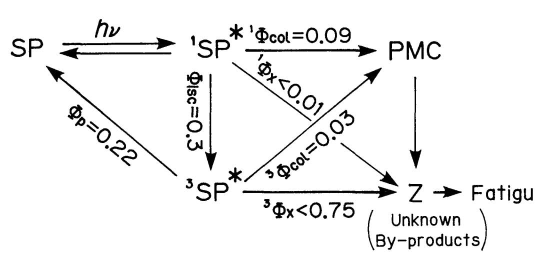
Relative Coloration Efficiency through the Triplet State. The quantum yield (ϕ_{col}) for the coloration of **1** in acetonitrile was estimated to be ca. 0.1. Since ϕ_{col} is the sum of the contributions from the excited singlet (^{1}SP*) and triplet state (^{3}SP*), an equation can be given:

$$^1\phi_{col} + {}^3\phi_{col} \times \phi_{isc} = 0.1, \tag{2}$$

where $^1\phi_{col}$, $^3\phi_{col}$, and ϕ_{isc} are the efficiencies for coloration of ^{1}SP* and ^{3}SP*, and for intersystem crossing of SP. Equation 3 can be derived from Eq. 1 as

$$^3\phi_{col}/(^1\phi_{col} + {}^3\phi_{col} \times \phi_{isc}) = 1/3. \tag{3}$$

By using a value of 0.3 for ϕ_{isc},[10] the values for $^1\phi_{col}$ and $^3\phi_{col}$ can be obtained from Eqs. 2 and 3 as 0.09 and 0.03, respectively. Therefore, it can be concluded that the photocoloration of **1** occurs in 90% through the excited singlet state and in 10% through the triplet state when directly excited. This was confirmed by laser photolysis studies.[9] The reaction processes are shown in Scheme 1. Only 3% of ^{3}SP* undergoes transformation into PMC. The radiative deactivation of ^{3}SP* to the ground state occurs with a probability of ca. 20% at 75 K.[10] Other deactivation processes may



involve a nonradiative decay to the ground state and chemical reactions other than the photo-transformation to PMC, the probabilities of these respective processes being unclear. Photo-fatigue products of **1** have not yet been satisfactorily identified.[3] The irradiation of a toluene solution of SP with 365-nm light afforded several degradation products with a wide range of polarities, as separated by silica-gel TLC. The UV spectrum of one of them agreed with that of 2-hydroxy-5-nitrobenzaldehyde. Acidic products were also found.

Factors Influencing the Fatigue. The fatigue of **1** in solution upon prolonged irradiation was shown to depend upon the polarity of the solvents. Figure 4 shows the half-life (min) of PMC as a function of Dimroth's E value of the solvent.[11] It can be seen that the half-life increases with increasing solvent polarity; for example, in hexane it is less than 1 min, while in acetonitrile it is more than 100 min. In halogenated solvents the photodurability is much lower than is expected from their E values.

It is likely that the strong intermolecular interaction in nonpolar solvents[12] may result in an acceleration of the fatigue. In terms of this connection the concentration dependence of the fatigue was examined. In Table 1 are listed the quantum yields for the disappearance of **1** (3×10^{-5}—1.2×10^{-3} M) upon 365-nm light irradiation in toluene. The quantum efficiency of photo-degradation of **1** increases with increasing concentration of the starting material.

In Fig. 5 are shown typical examples of the fatigue of **1** (2.7×10^{-5} M) during alternate irradiation of UV (365 nm) and VIS (580 nm) lights in polar (acetonitrile) and nonpolar (toluene) solvents under an argon atmosphere. Clearly, the fatigue proceeds more rapidly in toluene than in acetonitrile, similar to the case of prolonged UV irradiation. The number of alternate irradiation cycles to reduce the PMC absorbance to one half of its initial intensity (half-life cycle) is 4 and 25 in toluene and acetonitrile, respectively. The addition of benzophenone (2.7×10^{-2} M) to these solutions induced a considerable acceleration of the fatigue, the number of half-life cycles being less than 2 in both solvents. On the other hand, 1,1′-binaphthyl (7.9×10^{-3} M) retarded the fatigue significantly. In acetonitrile, for example, the number of half-life cycles in the presence of 1,1′-binaphthyl is two-times larger than that in its absence and several tens times larger than that in the presence of benzophenone. A number of compounds including

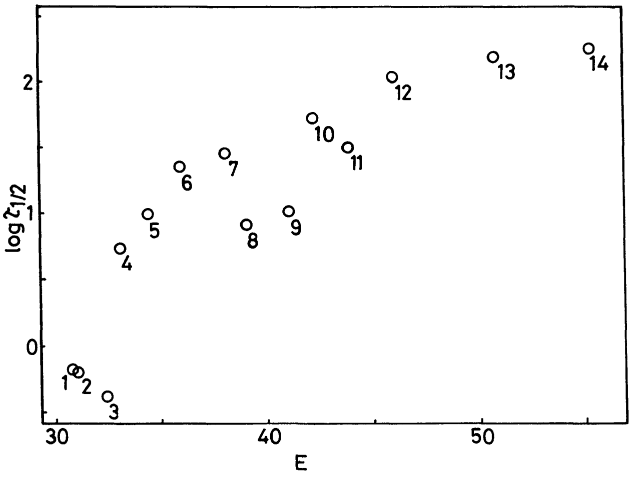


Fig. 4. The dependence of polarity of solvent for half-lives (min) of **1** on UV irradiation. [**1**]= 2.7×10^{-5} M. Irradiation light: 365 nm. 1: Hexane, 2: cyclohexane, 3: carbon tetrachloride, 4: toluene, 5: benzene, 6: dioxane, 7: ethyl acetate, 8: chloroform, 9: dichloromethane, 10: acetone, 11: N,N-dimethylformamide, 12: acetonitrile, 13: isopropyl alcohol, and 14: methanol.

Table 1. Concentration Dependence on the Fatigue of **1**

Concentration (M)	3×10^{-4}	6×10^{-4}	1.2×10^{-3}
Φ	2.1×10^{-3}	3.4×10^{-3}	4.8×10^{-3}

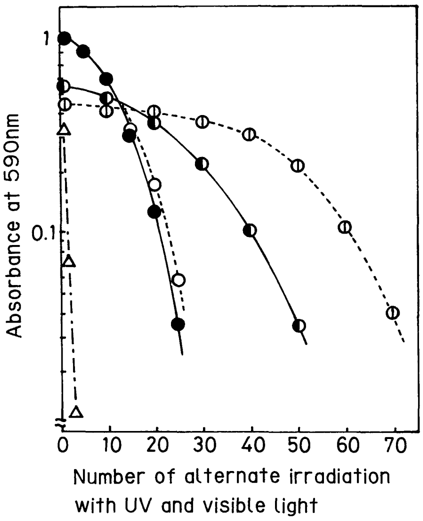


Fig. 5. Fatigue of **1** in the presence of triplet sensitizer or quencher. ●: **1** in toluene (2.7×10^{-5} M), ○: **1** (2.7×10^{-5} M)+1,1′-binaphthyl (7.9×10^{-3} M) in toluene, ◐: **1** in acetonitrile (2.7×10^{-5} M), ⦶: **1** (2.7×10^{-5} M)+1,1′-binaphthyl (7.9×10^{-3} M) in acetonitrile, and △: **1** (2.7×10^{-4} M)+benzophenone (2.7×10^{-2} M) in acetonitrile.

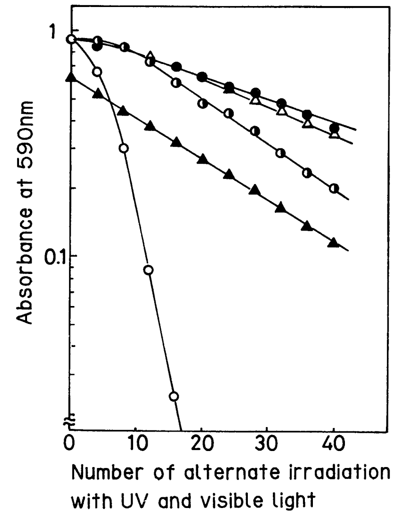
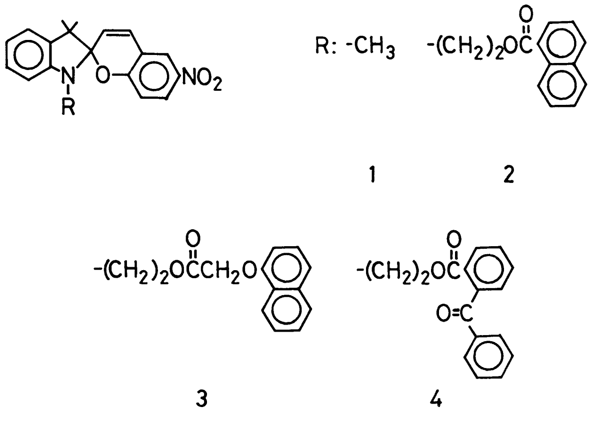


Fig. 6. Fatigue of **1** in the presence of DABCO. ○: [DABCO]=0, ◑: 2.7×10^{-4} M, ●: 2.7×10^{-3} M, △: 2.7×10^{-2} M, and ▲: 2.7×10^{-1} M.

amines and radical scavengers, like hydroquinone and phenols, were examined for fatigue. However, only the amines and the triplet quencher (binaphthyl) were effective in quenching the fatigue.

It has been found that amines are powerful for reducing fatigue. Figure 6 shows that 1,4-diazabicyclo[2.2.2]octane (DABCO) is potent for effectively enhancing the fatigue resistance in acetonitrile and toluene under an air atmosphere. It has been established that DABCO acts as a quencher of singlet oxygen.[13] However, another quencher of singlet oxygen, β-carotene, could not enhance the fatigue resistance. A similar effect was exerted by other amines, such as pyridine. Furthermore, it has also been observed that the fatigue is considerably accelerated by adding some acidic photo-degradation products of **1**. Therefore, the amines seem to act as neutralizing agents of acidic fragments which are accumulated during the photo-irradiation and interrupt the coloration of **1**.

Effects of Triplet Sensitizers and Quenchers Linked to the Spiropyran. Intramolecular effects were exerted on the fatigue of bichromophoric spiropyrans **2** and **3** possessing a naphthyl moiety and **4** with a benzophenone moiety as a side group. These spiropyrans showed an identical photochromism to that of **1**. The time profiles of fatigue of these compounds are shown in Fig. 7. It is clear that **2** and **3** are more resistant to fatigue than **1**, **4** being fatigue-labile. The half-life cycles of the former compounds are about two-times larger than that of **1**.



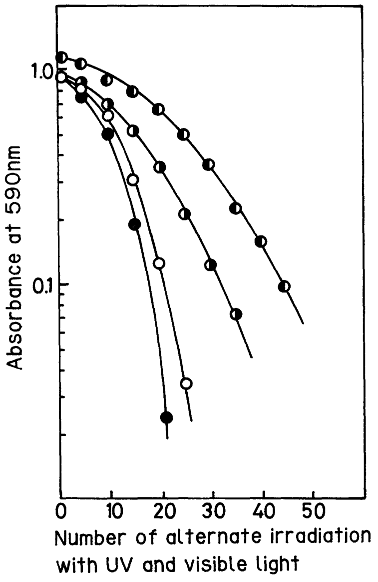


Fig. 7. Fatigue of **2**, **3**, and **4**. ○: **1**, ◑: **2**, ◐: **3**, and ●: **4**. Solvent=toluene. Concentration=2.7×10^{-5} M.

An intramolecular triplet energy transfer in these compounds was convinced by measurements of their phosphorescence spectra in EPA at 77 K. The results are shown in Fig. 8. Irradiation of **2** and **3** at 360 nm induced a phosphorescence from the naphthyl side group alone, though this chromophore has no absorption at this wavelength. The phosphorescence spectrum of **4** is totally identical to that of **1** and no emission from the benzophenone side group can be seen. For these systems, a possibility of intermolecular energy transfer would be excluded, because the phosphorescence spectrum of a solution of **1** and binaphthyl was identical to that of **1**.

Taking into account the intermolecular and intramolecular effects of the triplet quencher and sensitizer on the fatigue, it seems most likely that the fatigue is mainly due to chemical reactions through the triplet state. In contrast, the major reaction in the singlet state is the photocoloration, and the probability of the fatigue reaction is an order of magnitude less than that in the triplet state. Although the triplet state is not the sole channel to fatigue, the triplet quencher can protect **1** effectively from fatigue without any significant deletion of the coloration probability.

The acidic photo-degradation products of **1** inter-

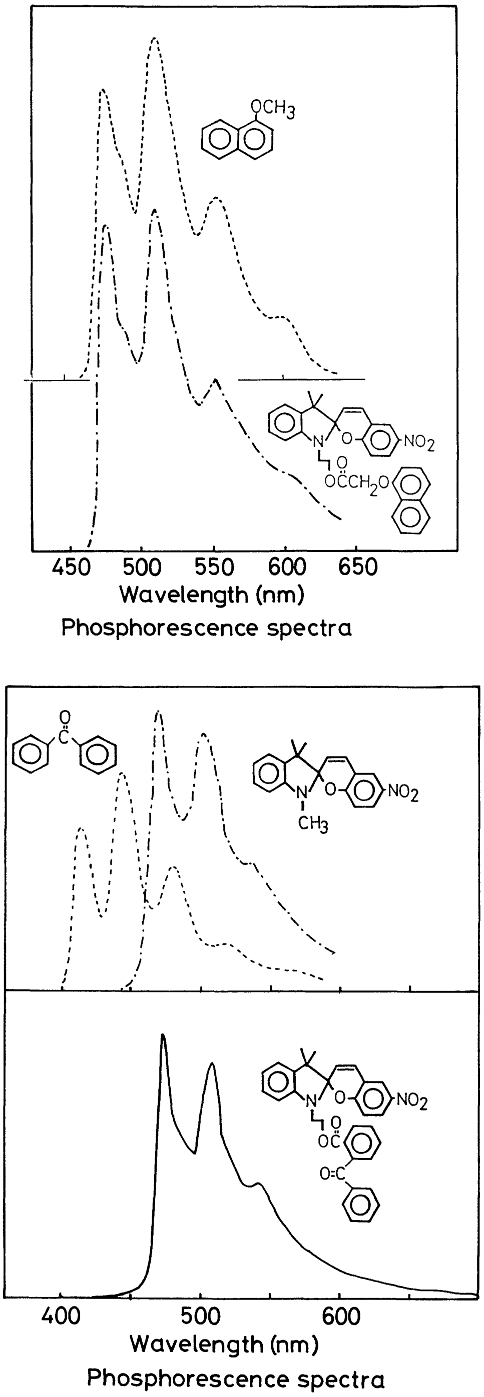


Fig. 8. Phosphorescence of spiropyrans.

rupt the coloration of **1**. The triplet quenchers do not affect their interruption. On the other hand, amines like DABCO seem to neautralize the acidic fragments and make them harmless. A detailed investigation on the role of DABCO is now under progress.

Experimental

Materials. 1′,3′,3′-Trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (1) was commercially available and crystallized from dichloromethane-hexane (mp 182—185 °C).

3,3′-Dimethyl-1′-[2-(1-naphthoyloxy)ethyl]-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (2). The mixture of 2,3,3-trimethyl-3*H*-indole (5 g, 31 mmol) and 2-bromoethanol (3.92 g, 31 mmol) was heated at 70 °C for 2 h with stirring. The viscous mixture was cooled to room temperature and washed with ammonia (50 ml). A separated yellow oil was extracted with diethyl ether and dried and evaporated. 1-(2-Hydroxyethyl)-3,3-dimethyl-2-methyleneindoline (**5**) was obtained as an oily product (4.8 g, 75%). 1′-(2-Hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (**6**) was obtained by condensation of **5** (2 g, 10 mmol) with 5-nitrosalicylaldehyde (1.64 g, 11 mmol) in boiling ethanol (50 ml) for 1.3 h. After filtration, the product was purified by further crystallization from ethanol (2 g, 51%, mp 176—177 °C). To a benzene solution of **6** (176 mg, 0.5 mmol), 1-naphthalenecarbonyl chloride (191 mg, 1 mmol) and pyridine (79 mg, 1 mmol) were added dropwise under cooling. The solution was further stirred for 3 h at room temperature. Pouring the solution into water, a crude solid was given and purified by silica chromatography to yield 96 mg of **2** (38% yield, mp 141—143 °C). ^{1}H NMR (CD_2Cl_2) δ=1.16 (3H, s, Me), 1.30 (3H, s, Me), 3.61—3.69 (1H, m, N-CH), 3.71—3.80 (1H, m, N-CH), 4.56 (2H, t, CH_2-O), 5.97 (1H, d, *J*=11 Hz, HC=C-Ph), 6.87 (1H, d, *J*=11 Hz, -C=CH-Ph), 6.70—8.85 (14H, m, aromatic H). Found: C, 73.12; H, 5.06; N, 5.87%. Calcd for $C_{31}H_{26}N_2O_5$: C, 73.50; H, 5.17; N, 5.53%.

3′,3′-Dimethyl-1′-[2-(1-naphthyloxyacetoxy)ethyl]-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (3). Condensation of **6** (166 mg, 0.5 mmol) with 1-naphthoxyacetic acid (202 mg, 1 mmol) in dichloromethane was carried out in the presence of *N*,*N*-dicyclohexylcarbodiimide (206 mg, 1 mmol) and 4-pyrrolidinopyridine (14.8 mg, 0.1 mmol). The solution was stirred for 3 h at room temperature. *N*,*N*-Dicyclohexylurea produced was filtered off. The filtrate was washed with 5% acetic acid and water and dried. The solvent was evaporated in vacuo and the product was recrystallized from hexane-dichloromethane to yield 126 mg of **3** (64%, mp 129—132 °C). ^{1}H NMR (CD_2Cl_2) δ=1.07 (3H, s, Me), 1.26 (3H, s, Me), 3.40—3.50 (1H, m, N-CH), 3.52—3.61 (1H, m, N-CH), 4.31—4.39 (1H, m, CH-O), 4.40—4.49 (1H, m, CH-O), 4.77 (1H, d, O=C-CH-O), 4.80 (1H, d, O=C-CH-O), 5.80 (1H, d, *J*=10 Hz, HC=C-Ph), 6.79 (1H, d, *J*=10 Hz, -C=CH-Ph), 6.51—8.35 (14H, m, aromatic H). Found: C, 70.70; H, 5.41; N, 5.49%. Calcd for $C_{32}H_{28}N_2O_6$: C, 71.90; H, 4.90; N, 5.28%.

1′-[2-(2-Benzoylbenzoyloxy)ethyl]-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (4). Condensation of **6** (88.4 mg, 0.25 mmol) with *o*-benzoylbenzoic acid (113.1 mg, 0.5 mmol) by the carbodiimide method gave 73 mg of **4** (52%, mp 150—153 °C). ^{1}H NMR ($CDCl_3$) δ=1.11 (3H, s, Me), 1.25 (3H, s, Me), 3.17—3.40 (2H, m, N-CH_2), 4.04—4.21 (2H, m, CH_2-O), 5.75 (1H, d, *J*=11 Hz, HC=C-Ph), 6.85 (1H, d, *J*=11 Hz, -C=CH-Ph), 6.65—7.99 (16H, m, aromatic H). Found: C, 72.84; H, 5.29; N, 4.84%. Calcd for $C_{34}H_{28}N_2O_6$: C, 72.85; H, 5.03; N, 5.00%.

Photo-Irradiation Measurements. Toluene and acetonitrile solutions containing **1**—**4** (2.7×10^{-4} M) with additives (0—3×10^{-2} M) were used for measurements of the photocoloration rates. The concentrations of **1**—**4** were so high that the solutions absorbed more than 90% of the incident light quanta. The solutions were deoxygenated by bubbling with argon gas and irradiated with a 500-W high-pressure mercury lamp. The irradiation wavelength was selected by the combination of a glass filter and a monochromator to be 313 nm for acetonitrile solutions and 365 nm for toluene solutions. The coloration rates during exposure to UV light were monitored at the wavelength of the peak maximum of PMC (555 nm in acetonitrile and 590 nm in toluene). The extinction coefficients at 313 nm in acetonitrile and at 365 nm in toluene were evaluated to be 8000 and 3900 for **1**, 80 and 72 for benzophenone, 3200 and 29 for xanthone, 220 and 14 for *p*-bromoacetophenone, and 440 and 15 for benzil. The quantum yield measurements for the photocoloration of **1** (5.4×10^{-4} M) in acetonitrile were done by using the 365 nm-light and a fulgide actinometry.[1)] After irradiation of an acetonitrile solution of **1** (2.8×10^{-5} M) with UV light, the absorbance of the solution at 555 nm was measured; at that time the concentration of SP was determined by HPLC. The absorption coefficient of PMC in acetonitrile at 555 nm was calculated to be $40000\pm2000\ \mathrm{l\,mol^{-1}\,cm^{-1}}$, which is consistent with the literature values.[14)]

For fatigue experiments, prolonged irradiation of solutions of **1**—**4** (2.7×10^{-5}—1.2×10^{-3} M) was carried out using two methods. One involved continuous irradiation with 365-nm light isolated from a 500-W mercury lamp with a glass filter. The other involved a UV (365 nm)-VIS (580 nm) alternating irradiator constructed with a 500-W mercury lamp, a collimating concave mirror, and two glass filters automatically exchangeable in selectable time intervals. Usually, the intervals were selected to be 10 and 30 s for UV and VIS irradiation, respectively, sufficient time periods for achieving the photostationary state. The half life of PMC bleaching was measured by observing the absorbances at 580 nm.

Phosphorescence measurements were carried out with a Hitachi MPF 4 spectrofluorometer at 77 K.

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