BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1730—1734 (1969)

Photoreversible Photographic Systems. VI. Reverse Photochromism of 1,3,3-Trimethylspiro[indoline-2,2′-benzopyran]-8′-carboxylic Acid

Isamu SHIMIZU, Hiroshi KOKADO and Eiichi INOUE

Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

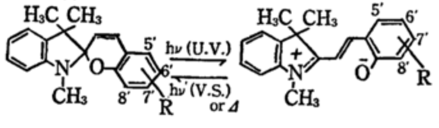
(Received June 17, 1968)

Many derivatives of 1,3,3-trimethylspiro[indoline-2,2′-benzopyran] (**1**) exhibit photoreversible color changes in organic solvents. One of the derivatives 1,3,3-trimethylspiro[indoline-2,2′-benzopyran]-8′-carboxylic acid (**2**) shows "reverse photochromism" in polar solvents. The compound **2** exhibits a deep color in the polar solvent and the color is bleached by irradiation with either visible or ultraviolet light. The color reappears thermally as the irradiation is ceased. The thermal conversion rate from the colorless form to the colored one depends on the solvents. On the other hand, the isomer 1,3,3-trimethylspiro[indoline-2,2′-benzopyran]-6′-carboxylic acid shows neither normal nor reverse photochromism under usual conditions, but exhibits reverse photochromism when acid such as malonic acid is added into the solution. The compound **2** is assumed to have a merocyanine dye-like structure due to the intramolecular proton transfer.

The photochromism of some derivatives of 1,3,3-trimethylspiro[indoline-2,2′-benzopyran] have been investigated by Fisher,[1] Lashkov,[2] Balny,[3] and the present authors.[4] It has also attracted the interest of workers in technological field photomemory, masking materials, optical switches and optical displays.

The ordinary photochromism of the spiran has been known for the conversion of a stable colorless state into a colored metastable state with ultraviolet light. The colorless modification is transformed from the colored one either spontaneously when the solution is stored in the dark, or by irradiation with visible light. The process that takes place in the photochromic system is presented as

(1)



A (colorless) B (colored)

R (**2**) -8′-COOH
(**3**) -6′-COOH
(**4**) -6′-NO_2
Δ heat

Some of these colorless photospirans are converted into colored forms when they are adsorbed on the solid surface such as silica gel or alumina, and the color can be bleached with visible light. This type of reversible photo-color change is called " reverse photochromism. " The authors have found that 1,3,3-trimethylspiro[indoline-2,2′-benzopyran]-8′-carboxylic acid (**2**) shows a reverse photochromism without adsorbents. The substance **2** exhibited intense color when it was dissolved in organic solvents. The color of the solution was diminished by irradiation with either visible or ultraviolet light. The colorless species was converted into the original colored one as the irradiation was ceased.

In this paper, the properties of the compound **2** are described in comparison with a colorless isomer 1,3,3-trimethylspiro[indoline-2, 2′-benzopyran]-6′-carboxylic acid (**3**). The effects of added acid or alkali on the solution of the compound **2** or **3** are also described.

Experimental

Absorption spectra with short life were obtained with a Hitachi Rapidscan Spectrophotometer SPR-2 which scanned from 200 mμ to 700 mμ within 0.15 sec. The other experimental procedures were given in other reports.[4,5]

Results and Discussn

The compound **2** is soluble in polar solvents, but not in non-polar solvents. The isomer **3**, however, is not soluble in polar solvents but soluble in non-

---

[1] R. Heiligmen-Rim, Y. Hirshberg and E. Fisher, *J. Phys. Chem.*, **66**, 2465 (1962).

[2] G. I. Lashkov and A. V. Shablye, *Opt. Spect*, **19**, 455 (1965).

[3] C. Balny and P. Douzou, *Compt. Rend.*, **262C**, 1235 (1966).

[4] I. Shimizu, H. Kokado and E. Inoue, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 2344 (1967).

[5] I. Shimizu, H. Kokado and E. Inoue, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem Sect.)*, **89**, 755 (1968).

polar solvents. The absorption spectra of the compound **2** and **3** in ethanol are shown in Fig. 1. The compound **2** exhibits an intense color which depends on the solvent, while the isomer **3** does not have any absorption band in visible region. The shape and the strength of the absorption band of the compound **2** in visible region is similar to that of the colored state of photospiran **4**. From the absorption spectrum and solubility, the compound **2** is assumed to have a merocyanine dye-like structure which is homologue of the colored state of the photospiran **4**.

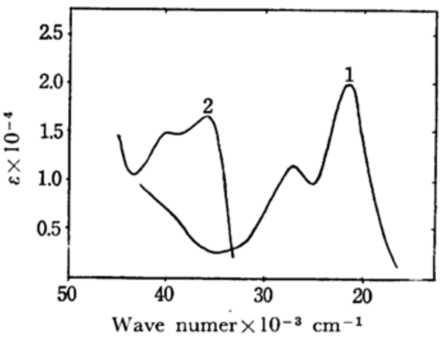


Fig. 1. Absorption spectra of **2** and **3** in ethanol.

1 Compound **2**
2 Compound **3**

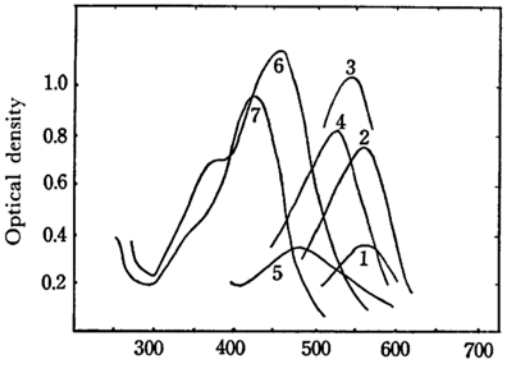


Fig. 2. Absorption spectra of **2** in various solvents.

1) ethyl acetate, 2) pyridine, 3) acetone,
4) acetonitrile, 5) *n*-butanol, 6) methanol,
7) water

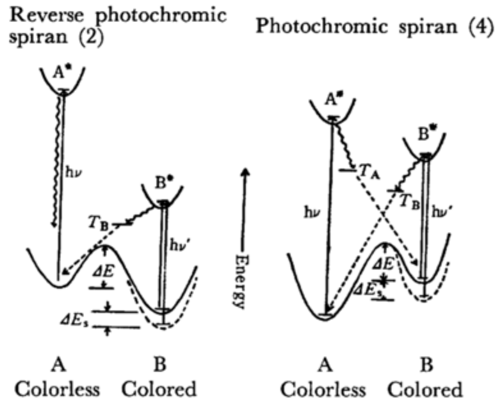


Fig. 3. Energy schemes which illustrate normal or reverse photochromism.

A*B*; excited state of A (B)
ΔE; activation energy for the reaction A→B or B→A
ΔE_S; stabilization energy
T_A,T_B; triplet state of A (B)

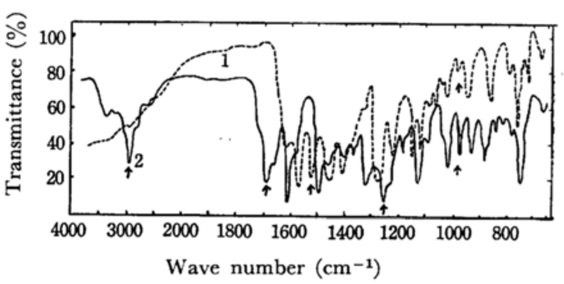


Fig. 4. IR spectra of **2** and **3** in KBr.

1) ······ compound **2**
2) —— compound **3**

The absorption spectrum of **2** in visible region is shifted towards shorter wavelength with the increase in a solvent polarity. Dependence of the spectral shift on the solvent as shown in Fig. 2 was elucidated by considering the dipole moment of the colored species. The ground state of the colored species **2** would be stabilized by interaction with the solvent dipole, but the first excited state would not be stabilized. The energy difference between ground and first excited state would then increase with increasing stabilization energy. This process is shown in Fig. 3 schematically.

The absorption spectra of **2** and **3** in infrared region are shown in Fig. 4. The ν(C=O) band of COOH in 1720 cm^{-1} was observed in **3** but not in **2**. An absorption band in 1525 cm^{-1} was, however, found in **2** and it was assigned to $\nu(CO_2^-)$. The spiran band at 954 cm^{-1} that had been reported by Schiele[6] was found to be much weaker for **3** than for **2**. The 1237 cm^{-1} band of **2** that had been assigned to be ν(C=C–O)[6] was shifted towards a longer wave number. It could be the electron transfer from C to O atom of the pyran ring which increased the charge density of the O atom.[6] This fact on IR spectra gives good support to the previous assumption that the colored species of **2** has a structure like a merocyanine dye in which the pyran ring is ruptured due to the internal proton transfer.

---

6) C. Schiele and G. Arnold, *Tetrahedron Letters*, **1967**, 1191.

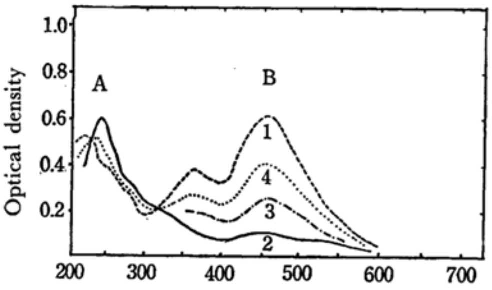


Fig. 5. The effect of irradiation on the ethanol solution **2** at room temperature.

1) Absorption spectrum of **2** in ethanol
2) After irradiation with light
3), 4) After standing the photo-bleached solution in the dark

It would be quite plausible to consider that the proton transferred structure is more favored because of energy.

The compound **2** in ethanol exhibited a deep color. The color was bleached with UV or visible light and the absorption band near the ultraviolet region was intensified. After the irradiation was stopped the color reappeared thermally. The absorption spectral changes are shown in Fig. 5. From the fact that the absorption spectrum of **2** in ethanol did not show any change at low temperature (−120 °C), the color change in the solution does not seem to be thermochromic. The photo-bleaching was performed utilizing visible light at −30°C. At this temperature, the thermal recovery to the colored one was not observed under the same condition. This behavior of the photo-bleached spiran (**2**) is quite the same as observed in the colorless spiran (**3**).

The thermal back reaction of **2** from the colorless state to the colored state followed the first order rate equation. The reaction rate depended on the solvent and the temperature. The temperature dependence of the rate constant in various solvents is shown in Fig. 6. The activation energies for the back reaction are presented in Table 1. The rate of thermal back reaction from colored to colorless state of photospiran (**4**) was determined in different solvents. The activation energy increased with the increasing solvent polarity. This results from the stabilization of meta-stable colored state of **4** by large polarity of the solvent. Thus, the higher the solvent polarity, the slower the thermal decoloration rate of compound **4**. On the other hand, the thermal recoloration rate of the compound **2** did not show any direct relationship with solvent polarity. This is understandable if we take into account the fact that the meta-stable form (colorless) of **2** is not sensitive. The energy scheme of the reactions are shown in Fig. 3. The colored state of spiran is assumed to have a zwitter ionic structure that is sensitive to added acid or alkali.

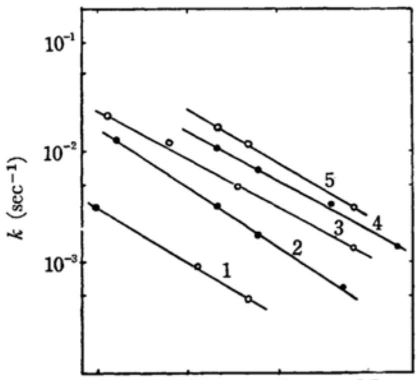


Fig. 6. Arrhenius plots for the recoloration rates of **2** in various solvents.

1) water, 2) pyridine, 3) ethanol, 4) acetone, 5) acetonitrile

TABLE 1. ACTIVATION ENERGIES FOR THE RECOLORATION OF THE COMPOUND **2**

Solvent	Activation energy kcal/mol
Water	22.6
Pyridine	25.4
Ethanol	20.2
Acetone	17.7
Acetonitrile	22.5

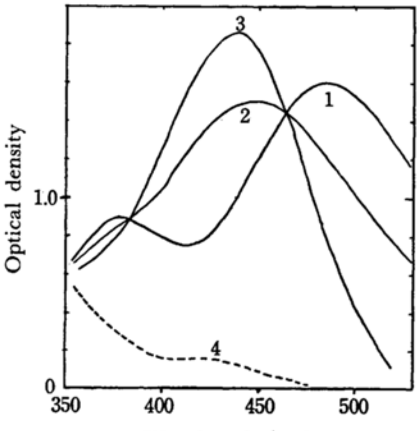


Fig. 7. Absorption spectra of **2** and malonic acid systems, and effect of irradiation with light on the systems.

1) Absorption spectrum of **2**; 7.0×10^{-5} mol/l
2) **2**; 7.0×10^{-5} mol/l+malonic acid; 1.0×10^{-3} mol/l
3) **2**; 7.0×10^{-5} mol/l+malonic acid; 9.4×10^{-2} mol/l
4) after irradiation 3) with light.

On addition of acid into the solution of **2** the absorption spectrum of the solution shifted to the shorter wavelength. The shift was proportional to the amount of added acid. The new colored species (C) produced by adding acid into the solution **2** was bleached by irradiation with UV or visible light. The color reappeared as the irradiation was stopped. The absorption spectral change in the reverse photochromic reaction is shown in Fig. 7. In ethanol solution of **2** the absorption band in visible region diminished quickly on addition of alkali. On the other hand, in aqueous solution the absorption band at longer wavelength (560 mμ) appeared as soon as the aqueous alkaline solution was added. The absorption band at 560 mμ decreased gradually at room temperature. The shape of the band was similar to that of the colored species of **2** in alcoholic solution. The absorption spectral changes with addition of alkali are shown in Fig. 8. The intermediate colored species was believed to have a merocyanine dye-like structure.

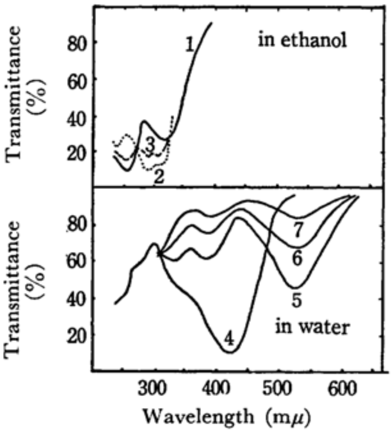


Fig. 8. The effect of added alkali on the absorption spectra of **2** in ethanol and water.

1) Absorption spectrum of **2** in ethanol just after ethanolic alkali was added
2), 3) After the solution 1) had been allowed to stand for 2 or 3 min
4) Absorption spectrum of **2** in aqueous solution
5) After aqueous alkali solution was added into 4)
6), 7) After the solution 5) had been allowed to stand in the dark for few minutes

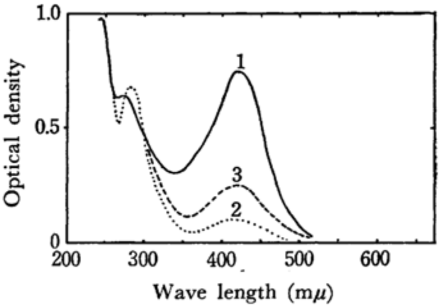


Fig. 9. The effect of irradiation with visible light on **2**: 6.7×10^{-5} mol/l, malonic acid; 1.0×10^{-2} mol/l, in ethanol.

1) Absorption spectrum of the system
2) After irradiation with visible light
3) After standing 2) in the dark for 5 min.

The solution of **3** in ethanol had an absorption band only near the ultraviolet region, and did not show any color change by irradiation with light even at a low temperature. As acid was added in the solution of **3** an absorption band in visible region appeared. The color was bleached by irradiation with visible light, but recovered thermally. The absorption spectrum of this colored species was

TABLE 2. QUANTUM YIELD OF THE PHOTOCONVERSION FROM COLORED SPECIES TO COLORLESS ONE

Compound	Quantum yield (ϕ)×ε	
	4358 Å	3650 Å
2	1.7×10^{-3}	1.3×10^{-3}
2 Malonic acid	9.0×10^{-3}	
3 Maleic acid	1.1×10^{-4}	1.1×10^{-4}

Solvent: ethanol
4358 Å, 3650 Å; irradiation light
ε; molar extinction coefficient of the colored species

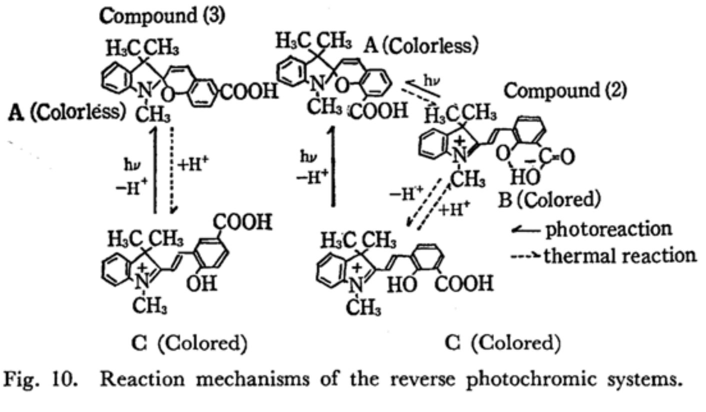


Fig. 10. Reaction mechanisms of the reverse photochromic systems.

similar to the colored species (C) of the compound **2**. The spectral change described above is shown in Fig. 9. The reaction mechanism of the reverse photochromism about the compound **2** and the system (compound **3**/acid) are shown in Fig. 10.

The photo-bleaching efficiencies of the compound **2** and the systems (compound **2**, or **3**/maleic acid) in ethanol are given in Table 2.

Conclusion

Depending on the nature and the position of substituted groups, the derivatives of 1,3,3-trimethylspiro[indoline-2,2-benzopyran] (**1**) differ from each other to a great extent in photochromic property. 1,3,3-Trimethylspiro[indoline-2,2′-benzopyran]-8′-carboxylic acid (**2**), shows a reverse photochromism. On the other hand, the isomer **3** which is substituted at 6′-position with COOH does not exhibit either the normal or reverse photochromism. As acid is added into the solution of the compound **3**, however, the system (compound **3**/acid) shows a reverse photochromism.