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Normal and Reverse Photochromism of 1-(β-carboxyethyl)-3,3-dimethyl-6′-nitrospiro[indoline-2,2′-2*H*-benzopyran] in Water–Dioxane

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Synopsis. The photochromism of 1-(β-carboxyethyl)-3,3-dimethyl-6′-nitrospiro[indoline-2,2′-2*H*-benzopyran] (I) was studied in water-dioxane. It was found that (I) exhibits normal photochromism in dioxane and reverse photochromism on addition of water to the solution.

A number of derivatives of 1-alkyl-3,3′-dimethylspiro [indoline-2,2′-2*H*-benzopyran] show photoreversible color change in organic solvents. Most of them are converted from a colorless stable state into a colored metastable state by irradiation with ultraviolet light. We have found that a photochromic compound, 1-(β-carboxyethyl)-3-3-dimethyl-6′-nitrospiro[indoline-2,2′-2*H*-benzopyran] (I), synthesized for chemical modification of enzymes, showed reverse photochromism in a water–dioxane mixture.

Experimental

Compound (I) was prepared by the reaction of 1-(β-carboxyethyl)-3,3-dimethylindolenium iodide and 5-nitrosalicylaldehyde in methyl ethyl ketone in the presence of piperidine, mp. 109.5—110.5 °C.

Absorption spectra were obtained with a Hitachi Rapidscan RSP–2 Spectrophotometer, the absorbances at λ_{max} being determined with a Shimazu Spectrophotometer UV–200 equipped with a thermostated cell compartment.

Results and Discussion

Variations of the absorption spectrum in the mixed solvents are shown in Fig. 1.

A colorless dioxane solution of (I) became violet after ultraviolet irradiation. The color faded very rapidly after the cessation of irradiation. In water–dioxane (water mole fraction of 0.34), compound (I) showed a weak absorption band at 566 nm before the ultraviolet irradiation (solid line 2), the absorbance increasing after the irradiation. At mole fraction 0.88, the solution of (I) showed an absorption band at 528 nm in the dark (solid line 3), the absorbance being reduced with the ultraviolet irradiation (dotted line 3). The absorption band reappeared spontaneously in the dark.

The difference in absorbance after and before the ultraviolet irradiation was determined in various water–dioxane mixtures. The results are given in Table 1.

It is clear that the difference in absorbance after (O.D.$_L$) and before (O.D.$_D$) the irradiation decreased with increasing mole fraction of water. Absorption maxima shifted toward shorter wavelengths with increasing solvent polarity.

Compound (I) exhibited reverse photochromism in formamide (Dimroth's solvent polarity value : E_t, 56.6),

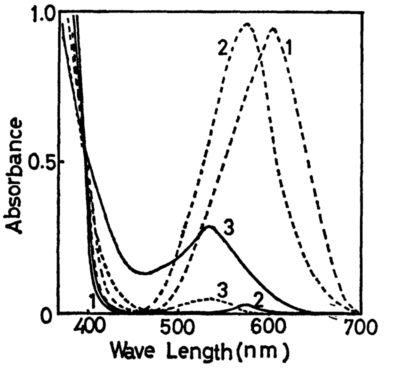

Fig. 1. Absorption spectra of (I) in water-dioxane (10^{-4} M).
—— before UV irradiation. ---- 10 s after UV irradiation. Mole fraction of water
1: 0, 2: 0.34, 3: 0.88.

TABLE 1. EFFECT OF WATER ON ABSORBANCE OF (I)
After 24 hr in the dark at 25 °C after preparation of the solutions (10^{-4} M)

Mole fraction of water	λ_{max} (nm)	O.D.$_L$[a) −O.D.$_D$[b)
0	600	+0.95
0.34	566	+0.965
0.54	552	+0.30
0.67	546	+0.22
0.76	540	+0.07
0.83	532	−0.09
0.88	528	−0.25

a) 10 s after UV irradiation. b) Before UV irradiation.

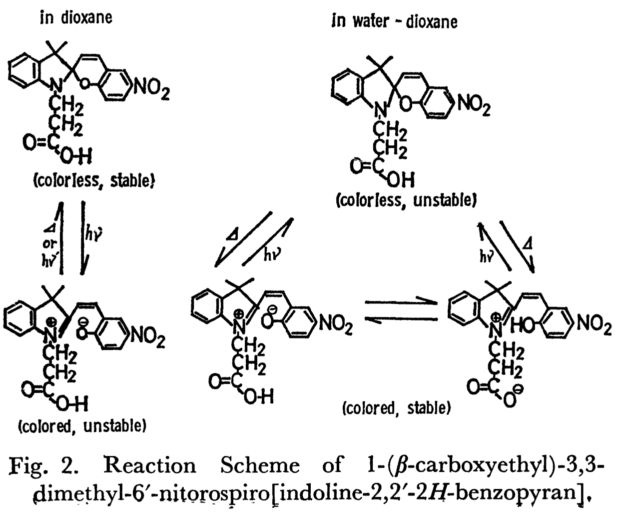

Fig. 2. Reaction Scheme of 1-(β-carboxyethyl)-3,3-dimethyl-6′-nitorospiro[indoline-2,2′-2*H*-benzopyran].

ethylene glycol (E_t, 56.3) and methanol (E_t, 55.5), but normal photochromism in other organic solvents having lower polarity such as ethanol (E_t, 51.9) and *n*-propanol (E_t, 50.7).

The results are attributed to the stabilization of ground state of the colored form due to the interaction with solvent.[1] At low mole fraction *ca.* 0.8, the ground state of the colored species was more unstable than that of the colorless species. Above 0.8, the increase of stabilization energy with the solvent might make the ground state of the colored species more stable than that of the colorless species, giving rise to reverse photochromism. The carboxyl group of (I) might play an important role in the reverse photochromism since 1,3,3-trimethyl-6′-nitrospiro[indoline-2,2′-2*H*-benzopyran] shows no remarkable effect in water–dioxane. The schemes are considered in Fig. 2.

Reference

1) I. Shimizu, H. Kokado, and E. Inoue, This Bulletin, **42**, 1726, 1730 (1969).