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Photochromism of Benzylviologens Containing Methyl Groups on Pyridinium Rings and Embedded in Solid Poly(*N*-vinyl-2-pyrrolidone) Matrix

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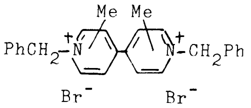
Synopsis. Benzylviologens with 2,2′- and 3,3′-dimethyl groups embedded in poly (*N*-vinyl-2-pyrrolidone) matrix indicate reversible photochromisms with absorption maxima at 605 and 775 nm under light, respectively, which are different from those (610, 570 nm) of conventional benzylviologens.

It is known that viologens embedded in solid poly (*N*-vinyl-2-pyrrolidone)(PVP) matrix undergo rapid reversible photoreductions in the air, which are clearly recognized by a deep color development ascribable to the formation of viologen radical cations (photochromism).[1,2]

The effect of the introduction of the methyl group in 2,2′- and 3,3′-positions of the pyridinium rings on the photochromic behavior of benzylviologens is the object of the present study.



2, 2′-Me **1**
3, 3′-Me **2**

Compounds **1** and **2** were prepared from 2,2′- and 3,3′-dimethyl-4,4′-bipyridyls, respectively, by the Menschutkin Reaction.

Figure 1 indicates the absorption spectra of PVP films containing viologens under exposure to UV light. Table 1 also gives data for photochromic behaviors of these films. Two remarkable features are recognized from these results. The absorption maximum for the colored form of **1**, *i.e.* radical cations, in Fig. 1 is located at 605 nm, which is almost the same as those for conventional viologen radical cations without ring substituents,[3] whereas that for **2** is remarkably red-shifted (775 nm) and the photosensitivity of **2** is lower than **1** (Table 1). This may indicate that the methyl substituents at 3 and 3′ positions of **2** hinder sterically the overlappings of the π-orbitals of the pyridine rings of viologen. The reason of the red-shift is unknown at present time, although the shape of curve III in Fig. 1 is somewhat different from II, which is a typical curve for viologen radical cation.[3] Another feature is that, in the absorption spectrum of the colored form of **1** (II in Fig. 1), no peaks for aggregated forms are recognized, whereas for conventional benzyl viologen dibromide (I) a distinct peak for the aggregated forms (570 nm)[3] is seen under the same film-forming conditions, there by indicating that the presence of 2,2′-methyl groups hinders the aggregation of viologen radical cations to a significant extent.

Accordingly, it is concluded that the introduction of simple methyl groups on the pyridinium rings of viologen dications brings about marked effects on the photochromic behavior in PVP matrix.

Table 1. Photochromic behaviors of compounds **1** and **2** in PVP matrix

Viologen	Irradiation[a] time/s	Absorption peak/nm	Absorbance[b] /mm^{-1}	Half-recovery[c] /min
Benzyl viologen dibromide	30	610 570[d]	4.82 —	30 —
1	30	605	4.42	20
2	60	775	2.65	30

a) At a distance of 10 cm from a 75W Hg lamp. b) Reduced to 1 mm of film thickness. c) Recoveries in the dark were complete for all films. d) Peak for aggregate.

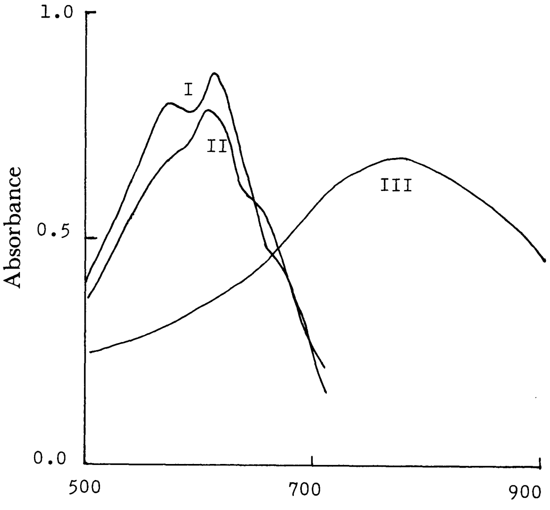


Fig. 1. Color development of viologens in PVP matrix under exposure to UV light.
I: Benzyl viologen dibromide, II: compound **1**, III: compound **2**.
Irradiations of films were carried out at a distance of 10 cm from a 75W Hg lamp. Irradiation times were 30, 30, and 60 s for I, II, and III, respectively.

Experimental

Infrared, ^{1}H NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, and Hitachi RMU-6 spectrometer, respectively, under standard conditions. Elemental analyses were carried out with a Perkin-Elmer 250 instrument.

2,2′-Dimethyl-4,4′-bipyridyl. A mixture of α-picoline (81 g, 0.87 mol) and sodium metal (1.0 g, 0.043 mol) was first stirred at 20 °C for 48 h with exclusion of moisture and then kept at 115 °C for 16 h. Oxygen was then bubbled through the mixture kept at 90 °C until the initial dark color disappeared (15 h). The reaction mixture was distilled to remove excess picoline, the residue was crushed to powder with addition of ether (50 ml), and water (2 ml) was added, followed by stirring for 10 min. Ether extraction was then made and the organic layer was dried over anhydrous sodium sulfate, followed by evaporation *in vacuo*. An excess of concd hydrochloric acid was added, the mixture was evaporated, and an equal volume of ethanol was added to the residue. Upon cooling in a refrigerator overnight, the resulting precipitate was filtered and washed with ethanol. Isolation of the product was done by dissolving the precipitate in water (10 ml) and then adding 1 M sodium hydroxide (1 M=1 mol dm^{-3}) solution (10 ml) and ether (50 ml) to effect extraction. The organic layer was washed with water, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The residue was recrystallized from benzene–hexane to afford crystals of mp 74—75 °C in 2% yield: Found: C, 78.24; H, 6.69; H, 15.07%. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.20%. IR (KBr) 3050 (aromatic), 3000—2900 (Me) cm^{-1}. NMR ($CDCl_3$) δ=2.6 (s, 6H, Me), 7.4 (d, 4H, pyridyl), 8.6 (d, 2H, pyridyl). MS (rel. intensity) 185 (M^+, 100).

3,3′-Dimethyl-4,4′-bipyridyl. The same procedure as that for the 2,2′-isomer was employed using β-picoline instead of the α-isomer to afford crystals of mp 120—122 °C in 2% yield: Found: C, 78.17; H, 6.63; N, 15.19%. Calcd for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.20%. IR (KBr) 3050 (aromatic), 3000—2900 (Me) cm^{-1}. NMR ($CDCl_3$) δ=2.1 (s, 6H, Me), 7.0 (d, 2H, pyridyl), 8.6 (d, 4H, pyridyl). MS (rel. intensity) 185 (M^+, 100).

1,1′-Dibenzyl-2,2′-dimethyl-4,4′-bipyridylium Dibromide (1). A solution of 2,2′-dimethyl-4,4′-bipyridyl (2.0 g, 13 mmol) and benzyl bromide (3.9 g, 26 mmol) in anhydrous acetonitrile (40 ml) was heated under reflux for 15 h. The resulting precipitate was filtered and recrystallized from methanol–ether to afford a pale yellow crystals in 87% yield. Found: C, 59.46; H, 4.95; N, 5.20%. Calcd for $C_{26}H_{26}N_2Br_2$: C, 59.33; H, 4.98; N, 5.32%. IR (KBr) 3050 (aromatic), 3000—2900 (CH_3, CH_2) cm^{-1}. NMR (D_2O) δ=3.0 (s, 6H, Me), 6.0 (4H, CH_2), 7.6 (m, 10H, Ph), 8.5 (t, 4H, pyridylium), 9.1 (d, 2H, pyridylium).

1,1′-Dibenzyl-3,3′-dimethyl-4,4′-bipyridylium Dibromide (2). The same procedure as that for **1** was employed using 3,3′-dimethyl-4,4′-bipyridyl instead of the 2,2′-isomer to afford a colorless crystalline powder in 87% yield. Found: C, 59.38; H, 4.89; N, 5.34%. Calcd for $C_{26}H_{26}N_2Br_2$: C, 59.33; H, 4.98; N, 5.32%. IR (KBr) 3050 (aromatic), 3000—2900 (CH_3, CH_2) cm^{-1}. NMR (D_2O) δ=2.3 (s, 6H, Me), 5.9 (s, 4H, CH_2), 7.6 (s, 10H, Ph), 8.1 (m, 2H, pyridylium), 9.0 (d, 4H, pyridylium).

Measurement of Photochromism. *(1) Film Preparation*: A solution of viologen (20 mg) and PVP (500 mg; MW 10000) in water (5 ml) was spread over a glass plate so as to cover an area of 1.2×2 cm. The glass plate was then stored in a desiccator ($CaCl_2$) overnight to make a transparent and almost colorless film. The films thus prepared were stored in a desiccator over saturated aqueous NaBr (RH, 58% at 20 °C) except for exposure to light and measurements of absorption spectra.

(2) UV-irradiation: Films were exposed to light at a distance of 10 cm from a 75 W mercury lamp (Toshiba SHL-100UV-2). Absorption spectra of the irradiated films were measured with a Hitachi 200-10 spectrophotometer. The absorbances thus obtained were reduced to values for 1 mm of film thickness.

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