Bull. Chem. Soc. Jpn., ***70***, *737—744 (1997)*

Photochromic, Electrochemical, and Photoelectrochemical Properties of Novel Azopyridinium Derivatives

Masaru Nakagawa,* Masahiro Rikukawa, Masayoshi Watanabe,† Kohei Sanui, and Naoya Ogata

Department of Chemistry, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo 102

†Department of Chemistry, Yokohama National University, Hodogaya-ku, Yokohama 240

(Received September 19, 1996)

Organic photochrome azopyridiniums were systematically prepared by quaternizing azopyridines with either dimethyl sulfate or 1,3-propanesultone. Photochemical, electrochemical, and photoelectrochemical studies on the azopyridiniums as methyl sulfate, hexafluorophosphate, and zwitterionic compounds were carried out in aprotic solvents and in aqueous solutions. The azopyridiniums, which have 3-located quaternized nitrogens to the azo group, exhibited photochemical activity of *trans* ⇆ *cis* isomerization. Quaternization of the pyridine moiety decreased the photochemical conversion between the *trans* and *cis* forms. The photochromic properties were influenced by an electronic effect of quaternized nitrogens and an electrostatic interaction of counter anions. In electrochemical studies, new redox-active azopyridiniums were found by using cyclic voltammetry and an electrochemical technique coupled with UV-vis spectroscopy. By the quaternization of azopyridines, the formal reduction potentials were shifted to a positive region up to −0.27 V vs. Fc/Fc^+. The reversibility of the electrochemical reactions was strongly dependent on the location of quaternized nitrogen. The *trans* ⇆ *cis* photoisomerization of electroactive azopyridiniums influenced their electrochemical properties. The photochromic molecules exhibited a photoelectric effect, which was a change in the cathodic limiting currents of azopyridiniums, reversibly modulated by ultraviolet light of an external stimulation.

Photo-switched molecular characters have been designed for the realization of molecular devices. The incorporation of photochromism and electrochromism into one molecule is a promising strategy for a photo-switched molecular system. Photoresponsible molecules consisting of an organic photochrome linked to a redox group provide prototypes of intramolecular chemical transducers whose electrochemical properties are modulated by an external optical stimulation.[1—11] The photo-induced isomerization of organic photochromes, such as diarylethenes and azobenzenes, is sufficiently large to enforce characteristic changes in the molecular physical and electrical properties.[12] Lehn et al. reported on photo-switched molecular wire using combined molecules of diarylethene and methylviologen.[1] The open forms of diarylethene, which lacked an electronic coupling of intramolecular pyridiniums, isomerized to closed forms having a bispyridinium polyene structure when ultraviolet light was irradiated. The resulting electronic coupling pyridiniums of closed forms exhibited redox activity. The combination of diarylethene and bispyridinium revealed the fact that the redox activity was controlled by the conversed states of photochrome. In contrast, the combination of diarylethene and hydroquinone realized electrochemically switched photochromes, whose photochromic activity was regulated by the electrochemical redox states between hydroquinone and quinone unit.[2] Electrochemically controlled photochromes were also reported by Saika et al.[3,4] The integration of *trans* ⇆ *cis* photoisomerized azobenzene and electrochemically active anthraquinone leads to electrochemically controlled photochromes. Electrochromic and photochromic arylazoanthraquinones have four distinct conversed molecular states caused by the multiplication of two redox states, quinone and hydroquinone, and two photoisomerized *trans* and *cis* forms. The thermal reaction rate of the oxidized *cis* form to the corresponding *trans* form is thirty-times as large as that observed for the *cis* form in the reduced hydroquinone state. As mentioned above, the photochromes linked to redox molecules are chemical transducers in molecular levels, promising the development of molecular devices regulated by the external stimulation of photons and electrons.

Photochrome azopyridines are versatile molecules for photochemistry[13,14] and electrochemistry.[15] Similar to azobenzenes, the aromatic azo groups also exhibit photo-induced geometrical *trans* ⇆ *cis* isomerization and undergo two single-electron-reductions in aprotic solvents. Another interest concerning azopyridines is to own pyridine moiety, which is chemically modified with protonation, alkylation,[16—18] and metallation.[19] In order to create new redox photochromes, which combine the structure of photochromic azobenzene and electrochromic methylviologen into one molecule, we prepared a series of azopyridinium methyl sulfates. The basic photochromic and electrochemical properties in CH_3CN and DMF were previously reported.[16] This paper deals with the photochromic properties of azopyridiniums with different anion species and molecular structures in CH_3CN and H_2O. The effect of counter-anion species on the photoisomerization of ionic photochromes was investigated. The photoelectrochemical properties caused by external light stimulation are also discussed.

Experimental

Apparatus and Procedures. Most chemicals were purchased from Wako Pure Chemicals Ltd. and used as received. Tetrabutylammonium perchlorate (TBAP) was purchased from Nacalai Tesque and used as received. CH_3CN for synthesis and electrochemical studies was dried (CaH_2 and P_2O_5) and distilled twice prior to use. *N,N*-Dimethylformamide (DMF) was dried (molecular sieves) and distilled. H_2O was purified through a Toraypure LV-10T. Azopyridines (**1**—**4**) were prepared according to the method of Campbell et al.[13] The syntheses of azopyridinium methyl sulfates (**5**—**10**), except for 1-methyl-4-(4-pyridylazo)pyridinium methyl sulfate **8**, were previously described in our paper.[16] Azopyridinium hexafluorophosphates (**11**—**14**) were obtained through anion-exchange reactions of ammonium hexafluorophosphate with the corresponding methyl sulfate salts. The zwitterionic azopyridiniums (**15**—**18**) were prepared through reactions of azopyridines with 1,3-propanesultone. The compounds were identified using ^{1}H NMR (JEOL GX-270, 270 MHz), FABMS (JEOL JMS-SX102A), and an elemental analysis.

UV-visible spectra were recorded on a Shimadzu UV-240 spectrometer. A 500 W high-pressure Hg lamp (Ushio Denki USH-250 D) was used to induce photoisomerization between the *trans* and *cis* forms of the azopyridines and azopyridiniums. The photoisomerization of the *trans* → *cis* form and the *cis* → *trans* form was induced by the irradiation of ultraviolet and visible light isolated by a glass filter (Toshiba UV-D33S and L-39). Electrochemical studies with cyclic voltammetry were performed in a three-electrode glass cell with a platinum disk working-electrode and a platinum wire counter-electrode. Spectroelectrochemical measurements were carried out using an optically transparent thin-layer electrode (OTTLE). The OTTLE has a suspended platinum mesh working-electrode in a fixed 0.33 mm-thick thin-layer. The spectroscopic measurements were performed with an Otsuka Denshi MCPD-1000 photodetector and a UP001 lamp power supply. All of the measurements were conducted under a deareated condition. The potentials were recorded versus the Ag/AgCl electrode (BAS), referenced to the ferrocene/ferrocenium couple (Fc/Fc^+) (+0.16 V vs. SCE).[20,21] A potentiostat (Hokuto HA301, Huso HECS 312B), a function generator (Hokuto HB104, Huso HECS 980), and an X–Y recorder (Rika-denki RW-21T, Riken F-35) were used.

In-situ photoelectrochemical measurements were conducted in an optically transparent quartz cell ($1\times1\times4$ cm) with a three-electrode configuration. The cell was maintained at 30 °C using a water bath with a thermostat. The reference-electrode Ag/Ag^+ was protected so as to avoid any influence of irradiation. A 10 μm-diameter platinum disk working-electrode and a 0.5 mm-diameter platinum disk counter-electrode were used.

1-Methyl-4-(4-pyridylazo)pyridinium Methyl Sulfate (8). A solution of freshly distilled dimethyl sulfate (0.19 g, 1.51 mmol) in benzene (5 ml) was added over a period of 2 h to a solution of 4,4′-azopyridine (0.60 g, 3.26 mmol) in benzene (5 ml). The reaction mixture was stirred for 2 d under a nitrogen atmosphere. Red precipitate was filtered off, washed (benzene and diethyl ether), dried and recrystallized from acetone to give 0.38 g (38%) of **8** as deep red prisms. Found: C, 46.2; H, 4.5; N, 18.3%. Calcd for $C_{12}H_{14}N_4O_4S$: C, 46.3; H, 4.5; N, 18.3%. ^{1}H NMR (D_2O) $\delta=9.09$ (2H, d, $J=6.7$ Hz), 8.88 (2H, d, $J=6.1$ Hz), 8.41 (2H, d, $J=6.7$ Hz), 7.98 (2H, d, $J=6.1$ Hz), 4.53 (3H, s), 3.76 (3H, s); FABMS: *m*/*z* 199 (M^+), 111 (M^-).

1-Methyl-3-phenylazopyridinium Hexafluorophosphate (11). A saturated aqueous solution of ammonium hexafluorophosphate was added to an aqueous solution (20 ml) of 3-phenylazopyridinium methyl sulfate **5** (0.50 g, 1.6 mmol) until no further precipitate was observed. The precipitate was filtered off, washed (H_2O), dried, and recrystallized from hot H_2O to give **11** (0.54 g, 98%) as red leaflets. Found: C, 42.0; H, 3.5; N, 12.1%. Calcd for $C_{12}H_{12}N_3PF_6$: C, 42.0; H, 3.5; N, 12.2%. ^{1}H NMR (acetone-d_6) $\delta=9.74$ (1H, s), 9.29 (1H, d, $J=6.1$ Hz), 9.10 (1H, d, $J=8.6$ Hz), 8.49 (1H, dd, $J=6.1$, 8.6 Hz), 8.06 (2H, d, $J=7.3$ Hz), 7.74—7.70 (3H, m), 4.83 (3H, s); FABMS: *m*/*z* 198 (M^+). The other hexafluorophosphate salts were also prepared as mentioned above.

1-Methyl-4-phenylazopyridinium Hexafluorophosphate (12). Red needles (98%, H_2O). Found: C, 41.9; H, 3.5; N, 12.3%. Calcd for $C_{12}H_{12}N_3PF_6$: C, 42.0; H, 3.5; N, 12.2%. ^{1}H NMR (acetone-d_6) $\delta=9.34$ (2H, d, $J=6.7$ Hz), 8.53 (2H, d, $J=7.3$ Hz), 8.12 (2H, d, $J=6.7$ Hz), 7.79—7.70 (3H, m), 4.73 (3H, s); FABMS: *m*/*z* 198 (M^+).

1,1′-Dimethyl-3,3′-azodipyridinium Bis(hexafluorophosphate) (13). Yellow needles (89%, H_2O). Found: C, 28.5; H, 2.8; N, 11.0%. Calcd for $C_{12}H_{14}N_4P_2F_{12}$: C, 28.6; H, 2.8; N, 11.1%. ^{1}H NMR (acetone-d_6) $\delta=9.87$ (2H, s), 9.39 (2H, d, $J=7.3$ Hz), 9.17 (2H, d, $J=4.3$ Hz), 8.55 (2H, dd, $J=4.3$, 7.3 Hz), 4.83 (6H, s); FABMS: *m*/*z* 214 (M^+).

1,1′-Dimethyl-4,4′-azodipyridinium Bis(hexafluorophosphate) (14). Red needles (93%, H_2O). Found: C, 28.6; H, 2.8; N, 11.0%. Calcd for $C_{12}H_{14}N_4P_2F_{12}$: C, 28.6; H, 2.8; N, 11.1%. FABMS: *m*/*z* 214 (M^+). ^{1}H NMR signals were too broad to identify the chemical structure of **14**.

3-(3-Phenylazopyridinio)propanesulfonate (15). 3-Phenylazopyridine **1** (0.50 g, 2.7 mmol) was dissolved in freshly distilled 1,3-propanesultone (16.5 g, 135 mmol). The solution was stirred for 1 d at 20 °C and for additional 6 h at 60 °C. The reaction mixture was precipitated in diethyl ether (100 ml). A yellow precipitate was filtered off, washed (diethyl ether) and dried in vacuo. The crude product was dissolved in methanol, and the filtrate was dropped into diethyl ether to give 0.67 g (82%) of **15** as a yellow powder. Found: C, 55.5; H, 5.0; N, 13.6%. Calcd for $C_{14}H_{15}N_3O_3S$: C, 55.1; H, 4.9; N, 13.8%. ^{1}H NMR (D_2O) $\delta=9.47$ (1H, s), 9.03 (1H, d, $J=6.1$ Hz), 8.95 (1H, d, $J=8.3$ Hz), 8.27 (1H, dd, $J=6.1$, 8.3 Hz), 8.03 (2H, dd, $J=1.8$, 8.0 Hz), 7.70 (1H, qui, $J=1.8$, 7.9 Hz), 7.68 (2H, dd, $J=1.8$, 7.9 Hz), 4.91 (2H, t, $J=7.3$ Hz), 3.08 (2H, t, $J=7.3$ Hz), 2.58 (2H, qui, $J=7.3$ Hz); FABMS: *m*/*z* 306 $(M+H)^+$. The other zwitterionic azopyridiniums were also prepared as mentioned above.

3-(4-Phenylazopyridinio)propanesulfonate (16). Red powder (70%). Found: C, 55.4; H, 5.0; N, 13.4%. Calcd for $C_{14}H_{15}N_3O_3S$: C, 55.1; H, 4.9; N, 13.8%. ^{1}H NMR (D_2O) $\delta=9.10$ (2H, d, $J=6.1$ Hz), 8.37 (2H, d, $J=6.1$ Hz), 8.11 (2H, d, $J=1.8$, 6.7 Hz), 7.73 (1H, qui, $J=6.7$ Hz), 7.72 (2H, d, $J=6.7$ Hz), 4.87 (2H, t, $J=7.3$ Hz), 3.07 (2H, t, $J=7.3$ Hz), 2.55 (2H, qui, $J=7.3$ Hz); FABMS: *m*/*z* 306 $(M+H)^+$.

3,3′-(3,3′-Azodipyridinio)bis(propanesulfonate) (17). Yellow powder (62%). Found: C, 44.7; H, 4.7; N, 13.2%. Calcd for $C_{16}H_{20}N_4O_6S_2$: C, 44.9; H, 4.7; N, 13.1%. ^{1}H NMR (D_2O) $\delta=9.63$ (2H, s), 9.10—9.15 (4H, m), 8.25 (2H, dd, $J=6.3$, 8.0 Hz), 4.94 (2H, t, $J=7.3$ Hz), 3.08 (2H, t, $J=7.3$ Hz), 2.58 (2H, qui, $J=7.3$ Hz); FABMS: *m*/*z* 429 $(M+H)^+$.

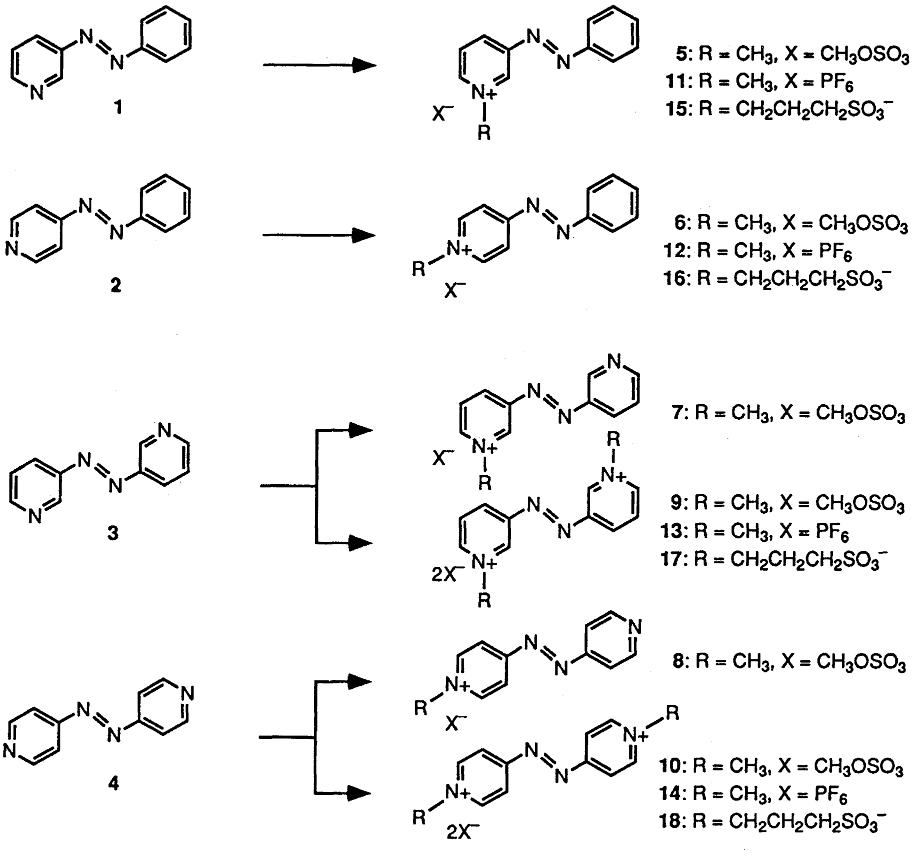
3,3′-(4,4′-Azodipyridinio)bis(propanesulfonate) (18). Pale red powder (92%). Found: C, 45.0; H, 4.7; N, 12.9%. Calcd for $C_{16}H_{20}N_4O_6S_2$: C, 44.9; H, 4.7; N, 13.1%. ^{1}H NMR (D_2O) $\delta=9.29$ (4H, d, $J=7.2$ Hz), 8.57 (4H, d, $J=6.7$ Hz), 4.96 (2H, t, $J=7.3$ Hz), 3.09 (2H, t, $J=7.3$ Hz), 2.59 (2H, qui, $J=7.3$ Hz);

FABMS: *m*/*z* 429 $(M+H)^+$.

Results and Discussion

UV-visible Spectroscopic and Photochromic Properties. Our previous paper[16)] reported that ionic photochromes of 1-methyl-3-phenylazopyridinium methyl sulfate (**5**) and 1-methyl-3-(3-pyridylazo)pyridinium methyl sulfate (**7**) underwent mutual *trans* $\leftrightarrows$ *cis* isomerization when the CH_3CN solutions were irradiated with ultraviolet (300 nm $< \lambda <$ 360 nm) and visible light ($\lambda >$ 390 nm). For the other azopyridinium methyl sulfates, no *trans* → *cis* photoisomerization was observed. A comparison of the *trans* → *cis* conversion percentage at the photostationary states of azopyridines and the corresponding azopyridinium methyl sulfates indicated that the substitution of electron-drawing nitrogen and quaternized nitrogen atom on the aromatic rings decreased the conversion of *trans* → *cis* photoisomerization. The 4-located nitrogen to azo moiety affected the photoisomerization more than did the 3-located nitrogen. The electronic effect of nitrogens on the azo moiety was supported by FT-Raman analyses of the symmetrical azo stretching mode.[16)] Another possibility of decreasing the photochromic properties is considered to be the existence of a counter anion, since the azopyridiniums are ionic photochromes. In order to investigate the photochemical properties of ionic photochromes, two additional types of azopyridiniums were prepared in this study and investigated with regard to the mutual *trans* $\leftrightarrows$ *cis* photoisomerization. One type of azopyridiniums comprises hydrophobic hexafluorophosphate salts instead of the hydrophilic methyl sulfate anion. Another type is a zwitterionic compound obtained by the reaction of azopyridines and 1,3-propanesultone. The covalently bonding anion structure achieved by the zwitterionic compounds enables a weakening of the electrostatic interaction between the azopyridinium cation and the counter anion.

The characteristic π–π^* and n–π^* absorption bands and the conversion percentages at the photostationary state of the azopyridines and azopyridiniums (Scheme 1) in CH_3CN and H_2O are summarized in Table 1. The *trans* → *cis* conversion percentages of 3-phenylazopyridiniums in CH_3CN solutions were the highest, 46%, for the zwitterionic **15**, 41% for the hexafluorophosphate **11**, and 39% for the methyl sulfate **5**. The effect of the anion species on *trans* → *cis* conversion was also observed in 1,1′-dimethyl-3,3′-azodipyridiniums, **9** and **13**. The π–π^* absorption bands were less affected by the anion species, while a red shift (Δ = 24 nm) of the n–π^* absorption band was observed for **11** and **15** compared with **5**. The conversion percentages of *trans* → *cis* isomerization were changed. No significant change in the n–π^* absorption bands of 4-phenylazopyridiniums and 4,4′-azodipyridiniums was observed in CH_3CN solutions. The reason for the characteristic n–π^* bands observed for methyl sulfate salts is a contribution of the hydrophilic methyl sulfate anion. The n–π^* band of **5** is presumably affected by an electrostatic



Scheme 1.

interaction of the methyl sulfate anion. In CH_3CN solutions, the methyl sulfate anion and azopyridinium cation form an ion pair, which decreases the photochromic activity of the azopyridiniums.

In order to prove that hydrophilicity of the methyl sulfate anion caused the lower *trans* → *cis* conversion, the two characteristic absorption bands and the *trans* → *cis* photochromic conversion of the azopyridiniums were measured in aqueous solutions. 3-Phenylazopyridiniums **5**, **11**, and **15** have the same π–π^* and n–π^* absorption bands, centered at 323 and 439 nm, and their photochemical *trans* → *cis* conversions were almost consistent. These same characters of the absorption bands and *trans* → *cis* conversions in aqueous solution indicate that an ion pair was formed from the cationic azopyridiniums and anionic methyl sulfates in CH_3CN solutions, and the *trans* → *cis* photoisomerization of azopyridinium methyl sulfates in CH_3CN was influenced by the formation of an ion pair.

Electrochemical Properties in Aprotic Solvents. Figure 1 shows cyclic voltammograms of 1 mmol dm^{-3} azopyridiniums in DMF containing 0.1 mol dm^{-3} TBAP as a supporting electrolyte. Table 2 lists the reduction potentials of azopyridine **1**—**4** and azopyridinium methyl sulfate **5**—**10** in CH_3CN and DMF referenced to an Fc/Fc$^+$ redox couple. The electrochemical measurements of 1,1′-dimethyl-3,3′-azodipyridinium (**9**) and 1,1′-dimethyl-4,4′-azodipyridinium bis(methyl sulfate) (**10**) were only carried out in DMF solutions because of their poor solubility. The first and second formal reduction potentials of the azopyridinium methyl sulfates were observed in an approximately 0.6—1.0 V positive region, compared with the corresponding azopyridines. The two-electron reduced species observed for **6**, **8**, and **10** were stable, due to an electron-drawing effect of quaternized nitrogens on the para location of the azo group, while the dianions of the azobenzenes and azopyridines were generally irreversible, due to the strong basicity of the dianions.[15,22] The mono-quaternized **6** and **8** exhibited a couple of reversible redox waves in DMF, whose first $E_{1/2}$ were −0.82 and −0.71 V (vs. Fc/Fc$^+$), and whose second $E_{1/2}$ were −1.55 and −1.45 V, respectively. Symmetrically quaternized **9** and **10** provided single and double redox couples. Compound **10** ($E_{1/2} = -0.27$ V vs. Fc/Fc$^+$), like methylviologen, was reduced at potentials 1.0 V lower than azopyridine **4**. The first reduction potential of **10** was 0.6 V

Table 1. UV-vis Spectral and Photochromic Properties of Azopyridines (**1**—**4**) and Azopyridiniums (**5**—**18**) in CH_3CN and H_2O

Azopyridines					$CH_3OSO_3^-$ compound				
Compound	Solvent	λ_{max}/nm (log ε)		*trans* → *cis*	Compound	Solvent	λ_{max}/nm (log ε)		*trans* → *cis*
		π–π^*	n–π^*	conversion[a]			π–π^*	n–π^*	conversion
1	CH_3CN	317 (4.3)	444 (2.6)	59 %	**5**	CH_3CN	324 (4.3)	421 (2.7)	39 %
	H_2O	318 (4.2)	427 (2.6)	60 %		H_2O	323 (4.3)	439 (2.7)	47 %
2	CH_3CN	310 (4.2)	450 (2.4)	49 %	**6**	CH_3CN	336 (4.3)	472 (2.7)	0 %
	H_2O	310 (4.2)	450 (2.4)	0 %		H_2O	335 (4.2)	472 (3.3)	0 %
3	CH_3CN	315 (4.3)	448 (2.5)	58 %	**7**	CH_3CN	315 (4.3)	400 (2.6)	19 %
	H_2O	315 (4.3)	448 (2.5)	54 %		H_2O	312 (4.2)	442 (2.4)	39 %
					9	CH_3CN	301 (4.5)	421 (3.3)	0 %
						H_2O	301 (4.3)	448 (2.2)	18 %
4	CH_3CN	283 (4.3)	455 (2.4)	24 %	**8**	CH_3CN	289 (4.3)	465 (2.5)	0 %
	H_2O	283 (4.3)	455 (2.4)	20 %		H_2O	287 (4.2)	472 (2.2)	0 %
					10	CH_3CN	278 (4.4)	454 (3.7)	0 %
						H_2O	280 (4.3)	480 (2.4)	0 %
PF_6^- compound					Zwitterionic compound				
Compound	Solvent	λ_{max}/nm (log ε)		*trans* → *cis*	Compound	Solvent	λ_{max}/nm (log ε)		*trans* → *cis*
		π–π^*	n–π^*	conversion			π–π^*	n–π^*	conversion
11	CH_3CN	323 (4.3)	445 (2.7)	41 %	**15**	CH_3CN	323 (4.2)	445 (2.7)	46 %
	H_2O	324 (4.2)	440 (2.8)	47 %		H_2O	324 (4.3)	439 (2.7)	46 %
12	CH_3CN	336 (4.3)	469 (2.7)	0 %	**16**	CH_3CN	336 (4.1)	469 (2.7)	0 %
	H_2O	335 (4.3)	459 (2.8)	0 %		H_2O	337 (4.3)	463 (2.8)	0 %
13	CH_3CN	301 (4.3)	450 (2.9)	9 %	**17**	CH_3CN[b]	—	—	—
	H_2O	301 (4.2)	451 (2.5)	12 %		H_2O	301 (4.3)	449 (2.4)	18 %
14	CH_3CN	278 (4.4)	455 (2.8)	0 %	**18**	CH_3CN[b]	278	455	0 %
	H_2O	279 (4.3)	479 (2.4)	0 %		H_2O	282 (4.4)	486 (2.4)	0 %

a) Conversions indicate π–π^* absorbance ratios of $(A_t - A_p)/A_t$ after the irradiation of UV light (300 nm $< \lambda <$ 360 nm); $A_t = \pi$–π^* absorbance at *trans* form; $A_p = \pi$–π^* absorbance at photostationary state. b) Absorption maxima and extinction coefficient could not be determined due to poor solubility.

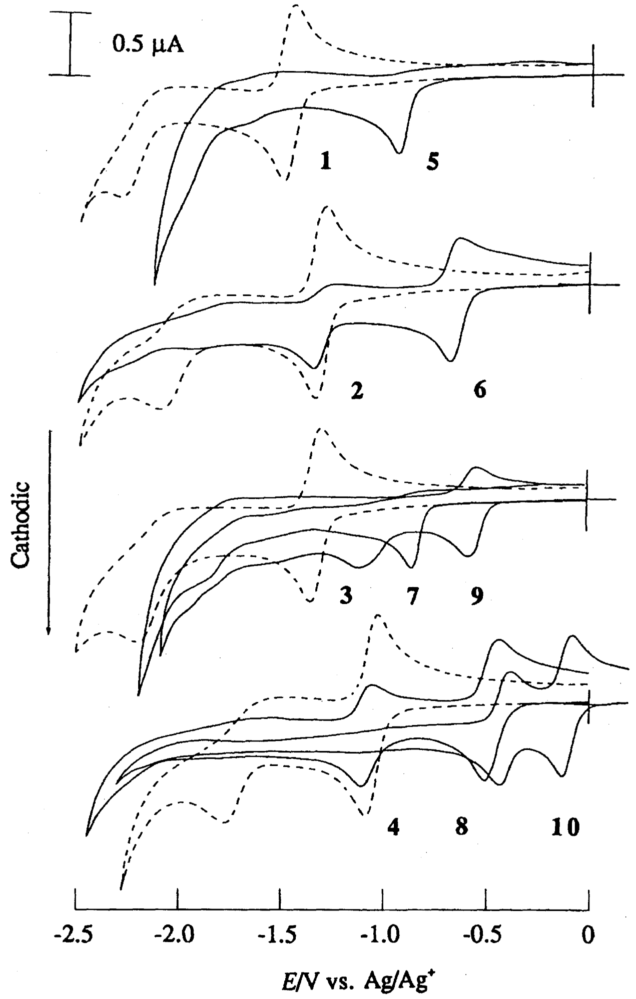


Fig. 1. Cyclic voltammograms ($v = 100$ mV s^{-1}, $r = 1$ mm) of 1 mmol dm^{-3} azopyridines (**1**—**4**) and azopyridinium methyl sulfates (**5**—**10**) containing 0.1 mol dm^{-3} TBAP in DMF. Reference electrode: Ag/Ag$^+$.

more positive than that observed for methylviologen chloride. Azodipyridinium **9**, having quaternized meta-located pyridine units, gave a reversible electrochemical property. Otherwise, the azopyridinium **5** and **7**, whose quaternized nitrogen was located in meta-position, gave an irreversible electrochemical reaction for the first reduction in aprotic solvents. These results are in contrast with ideas expressed in the previous paper concerning the reversible redox activities of aromatic azocompounds for the first reduction.[15,22] The first reduction potentials of **5** ($E_{1/2} = -1.07$ V vs. Fc/Fc$^+$) and **7** ($E_{1/2} = -0.98$ V vs. Fc/Fc$^+$) were approximately 0.6 V positive in contrast to those for the corresponding azopyridine **1** and **3**. The alkyl quaternization of azopyridines caused the electrochemical reduction potentials to shift to a positive region by 0.6—1.0 V, as described above. The reversibilities of the electrochemical reactions were strongly dependent on the location of quaternized nitrogens.

The visible absorption spectra of single-electron reduced azopyridiniums in aprotic solvents were measured by using spectroelectrochemical techniques in order to study the reversibility of the electrochemical reaction and to analyze the redox site for reduced species. Figure 2 shows visible absorption changes in a DMF solution of **10** during potential jumps. A visible absorption band in the range of 350 to 600 nm increased when a potential of −0.58 V (vs. Ag/AgCl), used to generate single-electron reduced **10**, was held for the electrolyte solution. The λ_{max} of a broad visible band shifted to 400 nm when a potential of −0.83 V to generate two-electron reduced **10** was held. These spectral changes were reversible after several electrochemical reduction and reoxidation processes. During the reduction of single-electron reduced **10**, an isosbestic point centered at 440 nm was observed. The spectroelectrochemical measurements suggested that compound **10** was highly electrochemically reversible up to the formation of dianion with a quinoid structure.

Table 2. Electrochemical Properties of Azopyridines (**1**—**4**) and Azopyridinium Methyl Sulfates (**5**—**10**) in CH_3CN and DMF

Compound	Solvent	1st reduction		2nd reduction	
		$E_{1/2}$[a]	I_{pa}/I_{pc}	$E_{1/2}$	I_{pa}/I_{pc}
1	CH_3CN	-1.58	0.96	-2.39	0.00
	DMF	-1.64	0.98	-2.42	0.00
2	CH_3CN	-1.42	0.85	-2.17	0.43
	DMF	-1.48	0.97	-2.20	0.02
3	CH_3CN	-1.49	0.95	-2.31	0.00
	DMF	-1.48	0.96	-2.35	0.00
4	CH_3CN	-1.23	0.93	-1.97	0.54
	DMF	-1.23	0.83	-2.01	0.04
5	CH_3CN	-0.99	0.18	-2.11	0.31
	DMF	-1.07	0.05	-2.14	0.03
6	CH_3CN	-0.74	0.86	-1.50	0.95
	DMF	-0.82	0.68	-1.55	0.63
7	CH_3CN	-0.91	0.22	-1.93	0.00
	DMF	-0.98	0.06	-1.99	0.01
8	CH_3CN	-0.65	0.88	-1.40	0.96
	DMF	-0.71	0.70	-1.45	0.80
9	DMF	-0.71	0.91	-1.31	0.29
10	DMF	-0.27	0.81	-0.58	1.10

[a] $E_{1/2} = (E_p + E_{p/2})/2$; E/V vs. Fc/Fc$^+$.

Figure 3 shows visible absorption changes in a DMF solution of **4** (top), **6** (middle), and **5** (bottom) during a potential jump to generate their single-electron reduced species. As can been seen in Fig. 3, a visible absorption band observed for single-electron reduced **5** was centered at 455 nm, and the sharp visible band no longer turned to the initial spectrum after the reoxidation process. For azopyridinium methyl sulfate **5**—**10**, the absorption bands almost centered at about 450 nm increased concomitantly with the single-electron reductions. The broad visible absorption spectra observed for **6**, **8**, and **10** were the same as those observed for reduced azopyridine **4**. However, the spectra of reduced **5** and **7** showed a sharp single visible absorption band. The cyclic voltammetry measurements of **3**, **7**, and **9** revealed that the

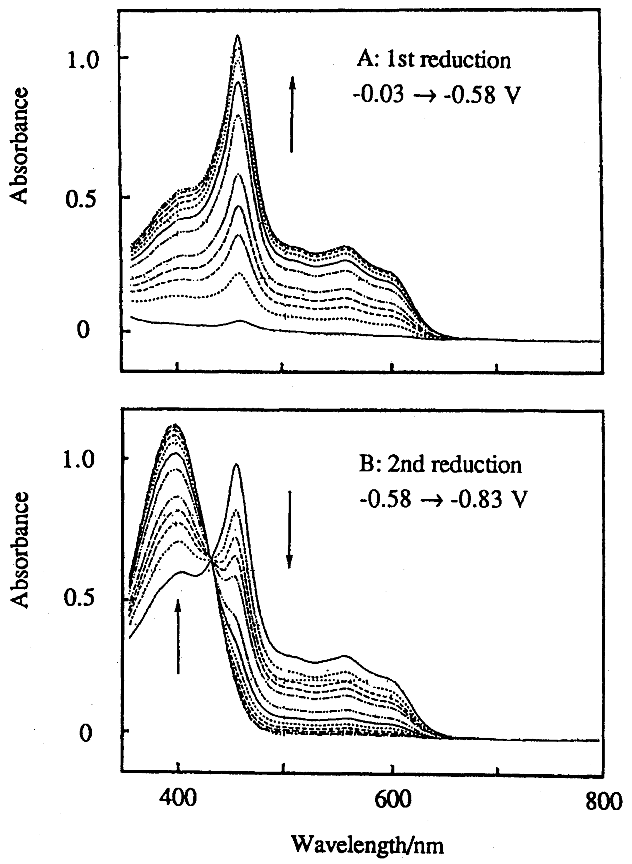


Fig. 2. UV-vis spectral changes in a 0.3 mmol dm^{-3} **10**/0.3 mol dm^{-3} TBAP/DMF solution during potential jumps. The potentials were recorded with Ag/AgCl, referenced to Fc/Fc$^+$.

quaternization of the pyridine moiety scarcely varied linearly their first reduction potentials. These electrochemical data indicate that the first reductions of **5** and **7** occurred in their pyridinium moieties, and that the reductions of the other azopyridiniums occurred in their azo moieties. The two-electron redox processes observed for **6**, **8**, and **10** were attributable to the formations of their stable quinoid structures by electron-drawing effects of quaternized nitrogens.

Photoelectrochemical Properties. Azopyridinium methyl sulfate **5** and **7** exhibited electrochemical and photochromic activity in the individual molecular unit. We investigated whether the electrochemical properties were modulated by mutual *trans* ⇆ *cis* photoisomerization of the azo moiety. Azopyridinium methyl sulfate **5**, **6**, and **7** were used for photoelectrochemical measurements, since the methyl sulfate salts were photochemically more stable than the hexafluorophosphate salts and the zwitterionic compounds.

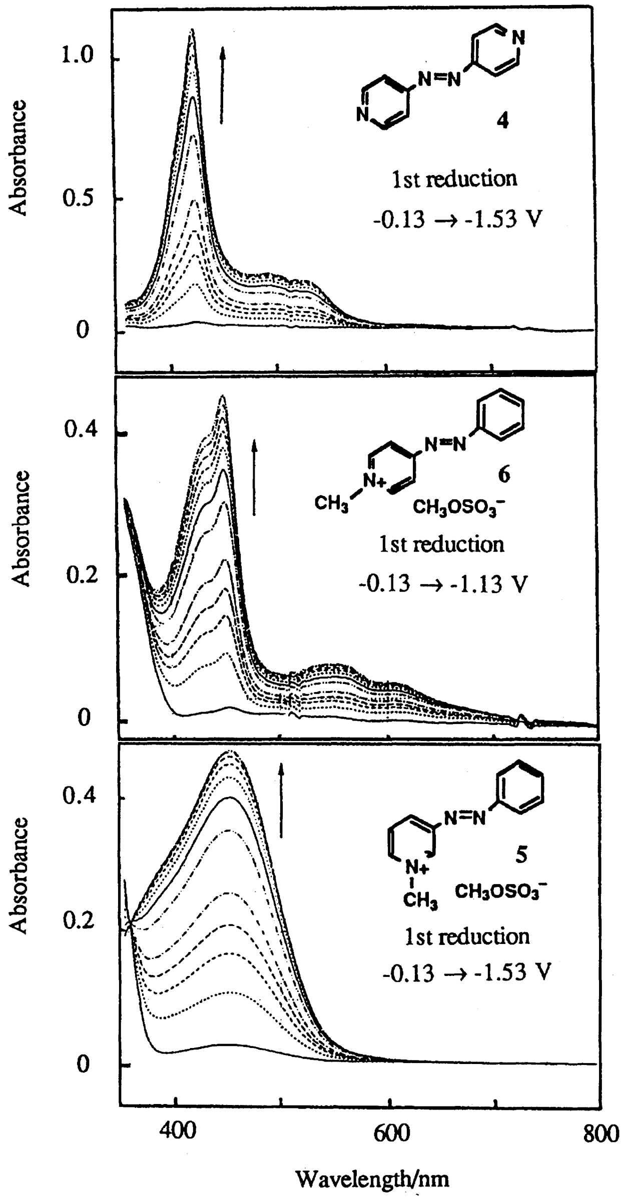


Fig. 3. UV-vis absorption spectral changes in 0.3 mmol dm^{-3} compound (**4**, **5**, and **6**)/0.3 mol dm^{-3} TBAP/DMF solutions during potential jumps. The potentials were recorded with Ag/AgCl, referenced to Fc/Fc$^+$.

Microelectrode voltammograms of the azopyridinium methyl sulfate **5**, **6**, and **7** are shown in Fig. 4. In the potential range of 0 to -1.1 V (vs. Ag/Ag$^+$), a reversible one-step reduction of **6** and irreversible reductions of **5** and **7** were observed. The reoxidation processes of the species accompanying a chemical reaction after electrochemical reduction were observed for **5** and **7** over the potential range of -0.5 to 0 V (vs. Ag/Ag$^+$). Steady-state limiting currents characteristic of microelectrode voltammetry were obtained on these reduction processes, indicating that the reduction of electroactive species was diffusion-limited. The steady-state cathodic currents of photoisomerizable **5** and **7** were increased by the irradiation of ultraviolet light (300 nm $< \lambda <$ 360 nm), while the cathodic current of **6** was less dependent on the UV irradiation. As shown in the inset of Fig. 4, the steady-state current of **5** and **7** gradually reverted to the original value after the UV irradiation was stopped. These results mean that the photoresponsive electrochemical characters were attributable to the photochromic *trans* → *cis* isomerization. The rate at which the current was reverted by stopping UV irradiation was on the same time scale as that of rapid thermal *cis* → *trans* isomerization within a minute.

The cathodic current of **5**, which increased due to the UV irradiation, was larger than that observed for **7**. The photoresponsive electrochemical characters were related to the conversion of the *trans* → *cis* form at the photostationary state, since the compound **5**, **7**, and **6** gave photochemical *trans* → *cis* conversion percentages of 39, 19, and 0%, respectively. For a reversible electron-transfer process, the steady-state limiting current was investigated and analyzed.[23] The limiting current of microelectrode varies linearly with the diffusion coefficient of redox species. Although our systems are irreversible in terms of electron-transfer processes, these results indicate that the photoelectrochemical responses of the steady-state limiting current are caused by the diffusive change. The photoisomerized *cis* form readily reached to the electrode due to the small molecular size. Azopyridinium **5** and **7**, which had both electrochemical and photochromic properties, exhibited photo-switched electrochemical properties modulated by geometrical *trans* ⇆ *cis* isomerization. These photoresponsive molecules are promising for molecular devices. Furthermore, the photo-regulated molecular dynamics will open up the development of photo-induced electron-carriers in pseudo-biological organizations.

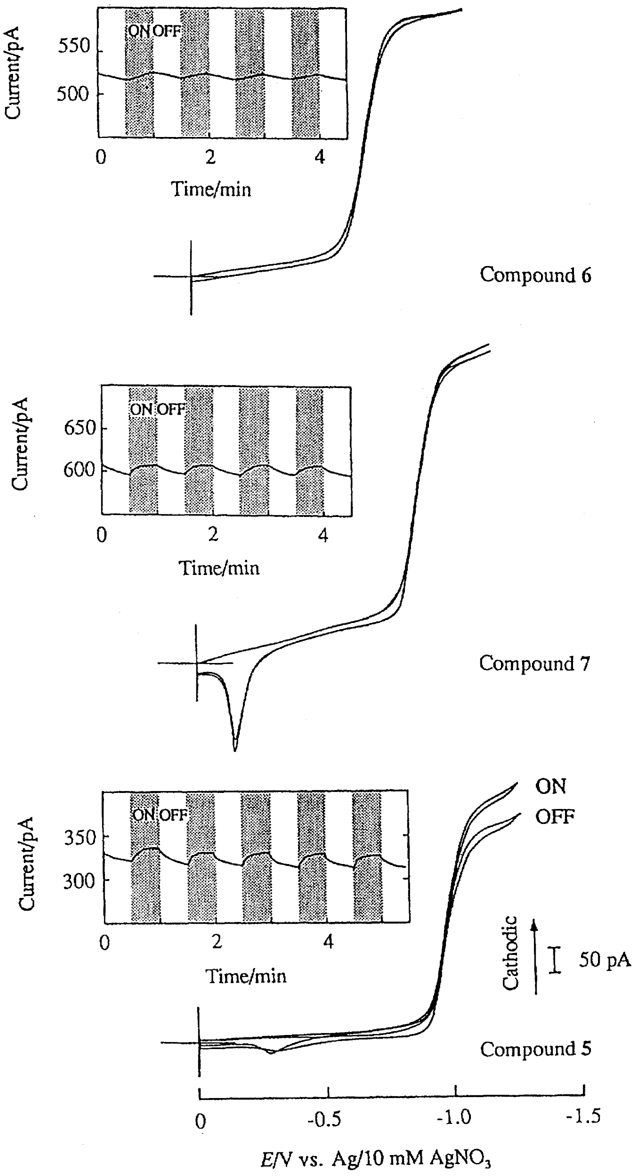


Fig. 4. Microelectrode voltammograms ($v = 50$ mV s^{-1}, $r = 10$ μm Pt disk) of 0.1 mmol dm^{-3} sample CH_3CN solutions irradiated with UV light (300 nm < λ < 360 nm). Inset: Current vs. time traces for 0.1 mmol dm^{-3} **5**, **6**, and **7** CH_3CN solutions irradiated with UV light at the first reduction potentials of compounds.

The authors are grateful for financial support from Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture and the Sasagawa Scientific Research Grant from the Japan Science Society. We gratefully acknowledge the assistance of Professor Kunio Shimizu of Sophia University for the OTTLE measurements. The authors thank to Professor Sumio Tokita of the University of Saitama and Professor Kunihiro Ichimura of Tokyo Institute of Technology for their helpful discussions.

References

1) S. L. Gilat, S. H. Kawai, and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, **1993**, 1439.

2) S. H. Kawai, S. L. Gilat, and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, **1994**, 1011.

3) T. Iyoda, T. Saika, K. Honda, and T. Shimidzu, *Tetrahedron Lett.*, **30**, 5429 (1989).

4) T. Saika, T. Iyoda, K. Honda, and T. Shimidzu, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 1181.

5) T. Saika, M. Irie, and T. Shimidzu, *J. Chem. Soc., Chem. Commun.*, **1994**, 2123.

6) J. F. Zhi, R. Baba, K. Hashimoto, and A. Fujishima, *Ber. Bunsenges. Phys. Chem.*, **99**, 32 (1995).

7) J. F. Zhi, R. Baba, K. Hashimoto, and A. Fujishima, *Chem. Lett.*, **1994**, 1521.

8) Z. F. Liu, K. Hashimoto, and A. Fujishima, *Nature*, **347**, 658 (1990).

9) Z. F. Liu, B. H. Loo, R. Baba, and A. Fujishima, *J. Electroanal. Chem.*, **270**, 437 (1989).

10) A. K. Newell and J. H. P. Utley, *J. Chem. Soc., Chem. Commun.*, **1992**, 800.

11) J. Achatz, C. Fisher, J. Salbeck, and J. Daub, *J. Chem. Soc., Chem. Commun.*, **1991**, 504.

12) "Photochromism, Molecules and Systems," ed by H. Dürr and H. Bouas-Laurent, Elsevier, Amsterdam (1990).

13) N. Campbell, A. W. Henderson, and D. Taylor, *J. Chem. Soc.*, **1953**, 1281.

14) E. V. Brown and G. R. Granneman, *J. Am. Chem. Soc.*, **97**, 621 (1975).

15) A. J. Bellamy, I. S. Mackirdy, and C. E. Niven, *J. Chem. Soc., Perkin Trans. 2*, **1983**, 183.

16) M. Nakagawa, M. Rikukawa, M. Watanabe, K. Sanui, and N. Ogata, *Chem. Lett.*, **1994**, 1785.

17) M. Nakagawa, M. Rikukawa, K. Sanui, and N. Ogata, *Supramol. Sci.*, **3**, 215 (1996).

18) J. E. Rockley and L. A. Summers, *Aust. J. Chem.*, **34**, 2683 (1981).

19) M. Rikukawa, D. Matuzaki, M. Nakagawa, K. Sanui, and N. Ogata, *Synth. Met.*, **71**, 2279 (1995).

20) R. R. Gagne, C. A. Koval, and G. C. Lisensky, *Inorg. Chem.*, **19**, 2854 (1980).
21) G. Gritzner and J. Kuta, *Electrochim. Acta*, **29**, 869 (1984).
22) J. L. Sadler and A. J. Bard, *J. Am. Chem. Soc.*, **90**, 1979 (1968).
23) J. Heinze, *Ber. Bunsenges. Phys. Chem.*, **85**, 1096 (1981).