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Electrochemical and Photochromic Properties of Azopyridinium Methylsulfates

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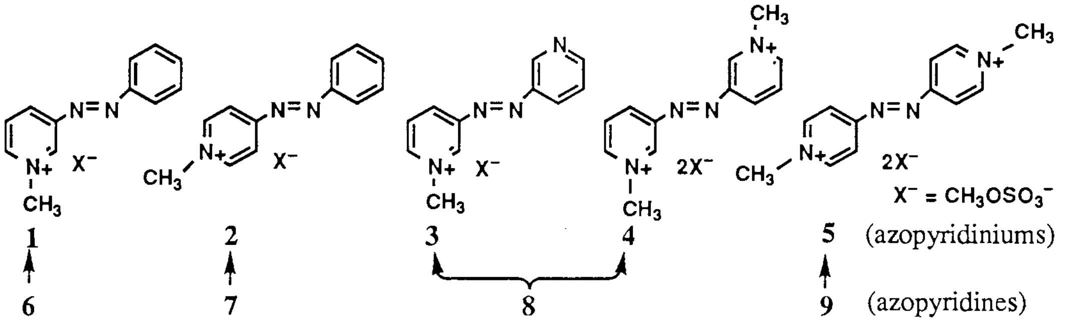
Azopyridinium methylsulfates were systematically prepared and their electrochemical and photochromic properties were evaluated by using UV spectroscopy and cyclic voltammetry. Some azopyridiniums were newly identified as photochromic compounds.

Photoresponsive molecules having electrochemical and photochromic activities are interesting materials for photoelectric molecular devices. Lehn et al. demonstrated the prototype of photoswitched molecular wires with diarylethene derivatives.[1] The open forms of diarylethenes are converted to the closed forms having bis-pyridinium polyene structure when irradiated with UV light, and the closed forms exhibit reversible redox activity. Shimizu et al. prepared electrochromic and photochromic arylazonaphthoquinones that showed interconversion of four distinct states caused by multiplication of two redox states, quinone and hydroquinone, and two photochromic geometrical isomers.[2] The *cis* form of quinone state can be thirty times as quickly reversed to the *trans* form as the *cis* form of hydroquinone state. These examples indicate that the molecules having both photochromic and redox activities are notable for developing photoresponsive molecular devices.

Photochromic molecules such as azobenzenes and stilbenes show reversible *trans* ↔ *cis* transformation induced by photo-irradiation, and various changes in the electron density, in the dielectric constant, and in the geometrical structure occur in the photochromic molecules.[3] If these photochromic changes could influence the electrochemical properties, the photoelectric transducer could be made to convert optical information to electrical information. In this article, we describe the preparations and the photochromic and electrochemical properties of azopyridiniums **1-5**.



Azopyridiniums **1-5** were prepared by methylation of corresponding azopyridines **6-9**,[4] according to the method of Campbell et al.[5] In a typical procedure, 3-phenylazopyridine **6** (2.1 g, 11 mmol) was dissolved in freshly distilled dimethylsulfate (27 g, 220 mmol) at room temperature, and the solution was stirred for 12 hours. The mixture was cooled until orange solid was precipitated. 3-Phenylazo-1-methylpyridinium methylsulfate **1** was recrystallized from acetone. The structures of these compounds were identified by using elemental analysis, ^{1}H-NMR, FAB-MS and FT-Raman.[6]

Table 1. UV spectral and photochromic properties of azopyridiniums (**1-5**) and azopyridines (**6-9**)

samples		λ_{max}/nm (logε) a) $\pi-\pi^*$	λ_{max}/nm (logε) a) $n-\pi^*$	conversion of *trans* → *cis* b)
azopyridiniums	**1**	324 (4.3)	421 (2.7)	28 %
	2	336 (4.3)	472 (2.7)	0 %
	3	315 (4.3)	400 (2.6)	19 %
	4	301 (4.5)	421 (3.3)	0 %
	5	278 (4.4)	454 (3.7)	0 %
azopyridines	**6**	317 (4.3)	444 (2.6)	59 %
	7	310 (4.2)	450 (2.4)	49 %
	8	315 (4.3)	448 (2.5)	58 %
	9	283 (4.3)	455 (2.4)	24 %

a) In CH_3CN. b) Conversions indicate the $\pi-\pi^*$ absorbance ratio of {A(trans) - A(photostationary state)}/A(trans) with UV irradiation ($\lambda > 290$ nm).

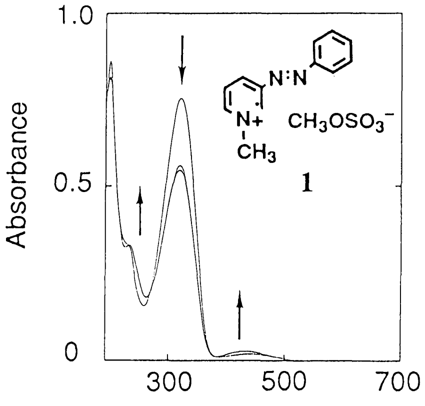


Fig. 1. UV spectral changes accompanying UV irradiation ($\lambda > 290$ nm) of **1** in CH_3CN.

The UV spectral and photochromic properties were summarized in Table 1. Figure 1 shows the UV spectral changes of **1** when a CH_3CN solution containing 40 μM of **1** was irradiated with a 500 W HP-Hg UV light through cut-off filters (Toshiba UV-29 and IRA-25S). With the photo-irradiation, the absorption band at 324 nm, assignable to *trans* π-π^* band, decreased concomitant with the increases of the absorption bands at about 260 nm and 421 nm, assignable to *cis* π-π^* and n-π^* bands, respectively. It was also found that the changed spectrum was reversed to the initial state when the solution was irradiated with Vis light (Toshiba L-39). In the dark, the changed spectrum was also quickly reversed to the original one within several seconds. These results indicate that this spectral change caused by the irradiation of UV light results from photochemical *trans* → *cis* isomerization of the azo moiety. A similar photochromic property was also observed in 3-(3'-pyridylazo)-1-methylpyridinium methylsulfate **3**, and the conversion of *trans* → *cis* isomerization for **1** was larger than that for **3**. The difference between the phenyl and the pyridyl group would cause the different conversion ratio between **1** and **3**.

Azopyridines also showed such a tendency. Compound **6** and 4-phenylazopyridine **7** with one pyridyl group could more turn to the *cis* form under UV light than 3,3'-azopyridine **8** and 4,4'-azopyridine **9** with two pyridyl groups, respectively. This means that the increase in the number of pyridyl group decreases the conversion of *trans* → *cis* isomerization. The pyridyl nitrogen atom located at 4-position made the conversion lower than that located at 3-position, in comparison with **6** and **7** or **8** and **9**. The conversion of the photoisomerization for **6** was highest in these azopyridines due to little effect of the pyridyl nitrogen on the azo moiety. Moreover this tendency was maintained in the quarternized azopyridiniums. The quarternized nitrogen was so electron-drawing that only **1** and **3** could photoisomerize, because of a little electronic effect of the quarternized nitrogens on the azo group. We concluded about the photoisomerization of azopyridines and azopyridiniums that the conversion of *trans* → *cis* photoisomerization was made lower as the electron-drawing atom was introduced into the aromatic rings in the photoisomerizable molecules. It was shown by the FT-Raman analysis of these compounds that one quarternized nitrogen located at 3-position had a little electronic effect on the azo moiety.

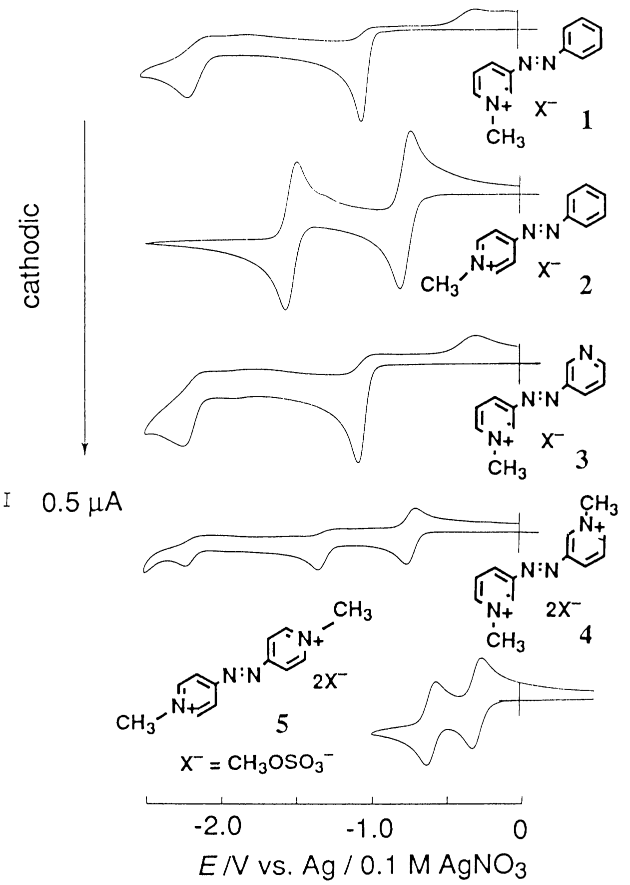


Fig. 2. Cyclic voltammograms (ν = 100 mVs^{-1}, r = 1 mm Pt disk) of 1 mM samples in CH$_3$CN or DMF (in case of **4** and **5**) containing 0.1 M (n-Bu)$_4$N$^+$ClO$_4^-$.

Figure 2 shows the cyclic voltammograms of 1 mM azopyridiniums in CH$_3$CN or DMF (in the case of **4** and **5** because of their poor solubility) containing 0.1 M (n-Bu)$_4$N$^+$ClO$_4^-$ as a supporting electrolyte. Compound **1** and **3** gave an electrochemically irreversible redox property for the first reduction in aprotic solvents. This contrasts with the previous paper on the electrochemical reversibility of aromatic azocompounds for the first reduction.7-8) The first reduction potentials of **1** ($E_{1/2}$: -1.00 V vs. Ag/Ag$^+$) and **3** ($E_{1/2}$: -0.92 V vs. Ag/Ag$^+$) were approximately 550 mV positive in contrast to the formal potentials of reversible reduction for **6** and **8** without methylation. Their first reductions were not likely to occur in their azo moieties but in their pyridinium moieties, because they were irreversible as general pyridinium salts and the first reduction potential of **3** was not linearly correlated with those of **8** and **4**. 4-Phenylazo-1-methylpyridinium methylsulfate **2** and 4,4'-azobis(1-methylpyridinium) methylsulfate **5** exhibited a couple of reversible redox waves, whose first $E_{1/2}$ were -0.75 V and -0.28 V and whose second $E_{1/2}$ were -1.51 V and -0.59 V (vs. Ag/Ag$^+$), respectively. These two-electron reduced species seemed stable due to the electron-drawing effect of quarternized nitrogens on the para position of azo group, while the dianions of azobenzenes and azopyridines were generally irreversible due to the strong basicity of dianions.7) Compound **5**, like methylviologen, was about 1000 mV more easily reduced than **9**. Its first and second reduction potentials were approximately 600 mV positive in contrast to those of methylviologen, and **5** would be an excellent electrochromic and electron-accepting molecule as methylviologens because of its electrochemical reversibility. Compound **4**, symmetrical structure, gave a reversible redox wave ($E_{1/2}$: -0.72 V vs. Ag/Ag$^+$) at the first reduction in DMF. It is interesting that bis-pyridinium structure **4** exhibits a reversible electrochemical property, in spite of the structure including meta located quarternized nitrogens. In these electrochemical experiments, we found that the reversible redox potentials of the novel redox molecules, **2**, **4**, and **5**, were higher than those of the corresponding azopyridines by 600 - 1000 mV.

We described the photochromic and electrochemical properties of some azopyridiniums having methylsulfate as counter anion. The photochemical *trans* ↔ *cis* isomerizations of **1** and **3** were observed in the CH_3CN solution. All of the azopyridiniums, **1-5**, were redox active, and **2**, **4** and **5** underwent reversible one-step or two-step reductions. The studies on the correlation between the photo-isomerization and the redox activity is now in progress.

References

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6) **1**: Reddish orange leaflets (acetone, 98%); Anal. Found: C, 50.3; H, 4.9; N, 13.6%, Calcd for $C_{13}H_{15}N_3O_4S$: C, 50.5; H, 4.9; N, 13.6%; ^{1}H-NMR (270 MHz, D_2O 4.80 ppm): δ 9.29 (1H, s, H-2), 8.88 (1H, d, *J* = 5.9 Hz, H-6), 8.85 (1H, d, *J* = 8.4 Hz, H-4), 8.19 (1H, dd, *J* = 5.9, 8.4 Hz, H-5), 7.98 (2H, dd, *J* = 1.5, 7.9 Hz, H-2'), 7.59-7.69 (3H, m, H-3', H-4'), 4.51 (3H, s, N-Me), 3.74 (3H, s, OMe); FT-Raman: 1633w, 1591m, 1492m, 1465m, 1445s(azo), 1187m, 1149s, 1029m (cf. **6**: 1442s(azo)); FAB-MS: m/z 198(M^+), 111(M^-).

2: Deep red prisms (acetone, 98%); Anal. Found: C, 50.3; H, 4.9; N, 13.6%, Calcd for $C_{13}H_{15}N_3O_4S$: C, 50.5; H, 4.9; N, 13.6%; ^{1}H-NMR: δ 8.93 (2H, d, *J* = 5.9 Hz, H-2), 8.25 (2H, d, *J* = 5.9 Hz, H-3), 8.02 (2H, d, *J* = 8.4 Hz, H-2'), 7.75-7.63 (3H, m, H-3', H-4'), 4.44 (3H, s, N-Me), 3.74 (3H, s, OMe); FT-Raman: 1639w, 1590w, 1487w, 1466m, 1439s(azo), 1176m, 1149s (cf. **7**: 1445s); FAB-MS: m/z 198(M^+), 111(M^-).

3: Red needles (acetone, 10%); Anal. Found: C, 46.5; H, 4.5; N, 18.1%, Calcd for $C_{12}H_{14}N_4O_4S$: C, 46.3; H, 4.5; N, 18.3%; ^{1}H-NMR: δ 9.44 (1H, s, H-2), 9.20 (1H, d, *J* = 1.2 Hz, H-2'), 8.96-8.98 (2H, m, H-4', H-6'), 8.75 (1H, d, *J* = 4.3 Hz, H-4'), 8.34 (1H, ddd, *J* = 1.2, 4.3, 7.9 Hz, H-6'), 8.25 (1H, dd, *J* = 6.1, 8.5 Hz, H-5), 7.70 (1H, dd, *J* = 4.3, 7.9 Hz, H-5'), 4.55 (3H, s, N-Me), 3.72 (3H, s, OMe); FAB-MS: m/z 199(M^+), 111(M^-).

4: Yellow needles (acetone/methanol, 70%); Anal. Found: C, 38.5; H, 4.7; N, 12.7%, Calcd for $C_{14}H_{20}N_4O_8S_2$: C, 38.4; H, 4.6; N, 12.8%; ^{1}H-NMR: δ 9.60 (2H, s, H-2), 9.04-9.08 (4H, m, H-4, H-6), 8.21 (2H, dd, *J* = 6.1, 7.9 Hz, H-5), 4.58 (6H, s, N-Me), 3.72 (6H, s, OMe); FT-Raman: 1639w, 1581w, 1505s, 1475s(azo), 1225m, 1054m (cf. **8**: 1447s); FAB-MS: m/z 214(M^+), 111(M^-).

5: Red needles (acetone/methanol, 80%); Anal. Found: C, 38.4; H, 4.5; N, 12.8%, Calcd for $C_{14}H_{20}N_{40}O_8S_2$: C, 38.4; H, 4.6; N, 12.8%; ^{1}H-NMR: δ 9.16 (4H, d, *J* = 5.0 Hz, H-2), 8.51 (4H, d, *J* = 5.0 Hz, H-3), 4.56 (3H, s, one of N-Me), 4.54 (3H, s, another of N-Me), 3.75 (3H, s, one of OMe), 3.73 (3H, s, another of OMe); FT-Raman: 1638w, 1524w, 1503m(azo), 1165s (cf. **9**: 1466s); FAB-MS: m/z 214(M^+), 111(M^-).

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