Synthesis and Properties of Novel Analogs of Viologen[1)]

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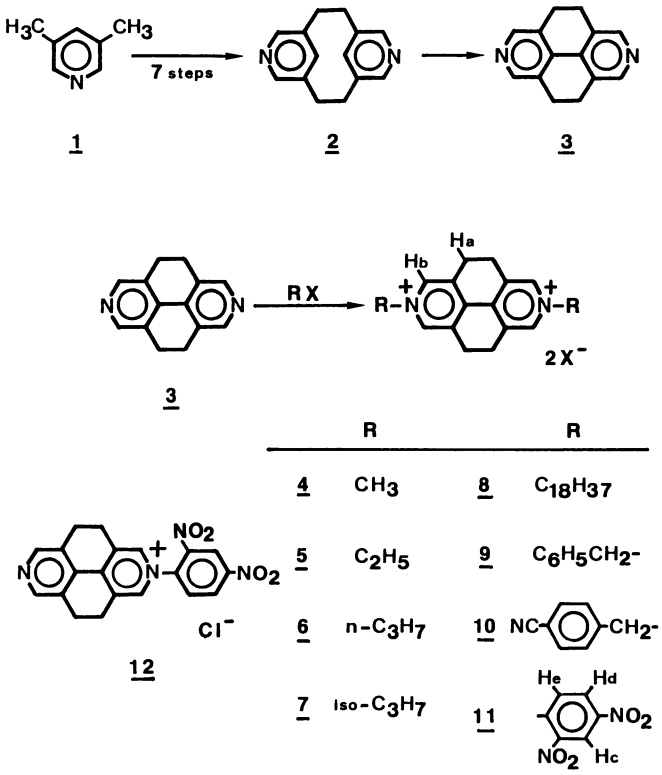
Several viologen analogs having good coplanarity were synthesized and their redox potentials were measured by cyclic voltammetry.

A viologen has attracted much attention in various fields as it shows two reversible one-electron reductions with very ease.[2)] Recently we reported synthesis and some properties of analog **4** of methylviologen(MV^{2+}), expecting that the increased resonance in the bipyridyl system may lower the redox potential.[3)] The present paper describes the syntheses of novel analogs of viologen **4**—**11** in detail and their electronic properties.



Scheme 1.

Results and Discussion

As described previously,[3)] [2.2](3,5)pyridinophane (**2**) was chosen as a starting material for our purpose. The compound **2** was prepared from the corresponding cyclic disulfone by pyrolytic procedure as reported.[4)] Pyridinophane **2** was converted into 4,5,9,10-tetrahydro-2,7-diazapyrene (**3**), a key intermediate for the following synthesis, by a transannular reaction. It is well-known that [2.2]metacyclophane is subject to the transannular reaction by treatment with various reagents, e.g. electrophiles, radical species, etc. to give tetrahydropyrene derivative.[5)] Pyridinophane **2**, on the other hand, was treated with these reagents but it produces none of the desired compound **3**. After various examinations, a modified transannular reaction with acetic anhydride, zinc dust, and $FeCl_3$ catalyst[6)] gave **3** in 53% yield, that corresponds to 2.1% in over-all yield from 3,5-lutidine (**1**). The structure of compound **3** was confirmed by elemental analysis and ^1H NMR spectroscopy. In the spectrum no other signal than two singlets (δ 2.87 and 8.39) was observed in $CDCl_3$. The former is assigned to H_a, a proton of ethylene bridge, and the latter to H_b, aromatic proton as shown in Scheme 1.

Quaternarization of **3** with alkyl halides was carried out in polar solvent, methanol or *N*,*N*-dimethylformamide (DMF), to yield the target compounds **4**—**11** in the conditions as shown in Table 1. For example,

Table 1. Reaction Conditions and Yield of Products **4**—**11**

Entry	Reagent	Solvent	Temp/°C	Time/h	Product	Yield/%
1	CH_3I	M[c)]	55—60	14.0	**4**	79
2	C_2H_5Br	D[d)]	95—100	3.0	**5**	87
3	C_3H_7Br	D	90—95	3.5	**6**	87
4	$(CH_3)_2CHBr$	D	100—105	3.0	**7**	68
5	$C_{18}H_{37}Br$	D	105—110	7.5	**8**	91
6	$C_6H_5CH_2Br$	D	105—110	13.0	**9**	Quant.
7	4-CBB[a)]	D	110—115	2.5	**10**	53
8	2,4-DNCB[b)]	M	Reflux	12.5	**11**	84
9	2,4-DNCB	M	50—55	7.0	**12**	60

a) 4-Cyanobenzyl bromide. b) 1-Chloro-2,4-dinitrobenzene. c) Methanol. d) DMF.

ethylation of **3** with ethyl bromide in DMF at 95—100 °C for 2 h gave 2,7-diethyl-4,5,9,10-tetrahydro-2,7-diazoniapyrene dibromide (**5**) in 87% yield. While arylation of **3** with 1-chloro-2,4-dinitrobenzene in methanol at 50—55 °C for 7 h gave mono-onium compound, 7-(2,4-dinitrophenyl)-4,5,9,10-tetrahydro-2-aza-7-azoniapyrene chloride (**12**) in 60% yield, the same reaction under reflux for 12.5 h afforded the desired bis-onium compound, 2,7-bis(2,4-dinitrophenyl)-4,5,9,10-tetrahydro-2,7-diazoniapyrene dichloride (**11**) in 84%. In the ^{1}H NMR spectrum of **11**, the aromatic proton appears at very low field (δ 9.35) in DMSO-d_6. The remarkable downfield shift of the aromatic protons is observed in all of the spectra of **4—11**, indicating the quaternarization of each two nitrogen atoms in the diazapyrene **3**. The redox potentials measured by cyclic voltammetry and the ^{1}H NMR characteristic shifts of **4—11** are summarized in Table 2.

Any cyclic voltammogram of the products **4—11** shows two reversible one-electron reductions except that of **11**. Cyclic voltammogram of **11**, on the other hand, shows diffusion-controlled and irreversible reduction, which is probably due to feature of nitro group. The redox potentials of **4—10** are almost equal to that of methylviologen in any case. This fact suggests that the increased resonance in the bipyridyl system and the electron-releasing effect of ethylene bridges are compensated each other in these diazoniapyrene derivatives **4—10**.

It is well-known that *N,N'*-bis(2,4-dinitrophenyl)-4,4'-bipyridinium salt is an available precursor for the other viologen derivatives by a facile ring transformation reaction with an amine.[7] From this point of view, the compounds **11** and **12** are assumed to be useful as valuable precursors for synthesis of a symmetrical and an unsymmetrical viologen analogs having good coplanarity.

Experimental

Measurements. All melting points were measured on a Yanako melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded with a Hitachi R-20B spectrometer, IR spectra with a Hitachi 260-10 spectrophotometer, and UV spectra with a Shimadzu UV-240 spectrophotometer. Cyclic voltammograms were obtained with a Yanako polarographic analyzer P-1100.

4,5,9,10-Tetrahydro-2,7-diazapyrene (3): To a mixture of 1.00 g (4.75 mmol) of [2.2](3,5)pyridinophane (**2**), 27 ml of acetic anhydride, 0.5 ml of acetic acid, and a catalytic amount of iron(III) chloride contained in a 100 ml three-necked flask was added a 136 mg portion of zinc powder(90% assay) with vigorous stirring at 30—40 °C under a nitrogen atmosphere. The temperature was maintained at 30—40 °C, an additional amount of zinc (1.362 g) was added in three portions at every half an hour. The mixture was stirred another 15 h at 30—40 °C, and then heated to 90 °C within 5 min. Upon ice-cooling to ca. 30 °C, stirring was continued further for 5 h under introduction of air. After evaporation, a little of water was added to the mixture and then neutralized till pH 9 with an aqueous solution of sodium hydroxide. The resulting mixture was stirred for additional 6 h at 40 °C. After filtration with Hyflo Super-Cel, the filtrate was extracted with chloroform. The organic layer was washed and dried over anhyd magnesium sulfate. The solvent was evaporated up to give a crystalline solid. It was purified by column chromatography on a silica gel to give 527 mg (yield: 53%) of **3**; colorless plates from acetone; mp 227.5—228.5 °C. ^{1}H NMR ($CDCl_3$) δ=2.94 (8H, s, benzylic CH_2), 8.39 (4H, s, aromatic H). Found: C, 80.98; H, 5.87; N, 13.33%; Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45%.

2,7-Dimethyl-4,5,9,10-tetrahydro-2,7-diazoniapyrene Diiodide (4): A solution of 118 mg (0.570 mmol) of 4,5,9,10-tetrahydro-2,7-diazapyrene (**3**) and 460 mg (3.2 mmol) of methyl iodide in methanol (5 ml) was stirred at 55 °C for 4 h. Then 460 mg (3.2 mmol, total 920 mg) of methyl iodide was added and the mixture was stirred for another 5 h. A red crystalline solid was collected by filtration and recrystallized from methanol to give 220 mg (yield: 79%) of **4** as red plates; mp>300 °C. UV(CH_3OH) 300 nm (log ε=4.14). ^{1}H NMR (DMSO-d_6) δ=3.19 (8H, s, benzylic CH_2), 4.37 (6H, s, CH_3), 9.06 (4H, s, aromatic H). Found: C, 38.76; H, 3.62; N, 5.59%; Calcd for $C_{16}H_{18}N_2I_2$: C, 39.05; H, 3.69; N, 5.69%.

2,7-Diethyl-4,5,9,10-tetrahydro-2,7-diazoniapyrene Dibromide (5): A solution of 120 mg (0.576 mmol) of **3** and 380 mg (3.46 mmol) of ethyl bromide in DMF (5 ml) was heated at 95—100 °C for an hour with magnetic stirring. After the addition of ethyl bromide (380 mg, 3.46 mmol), the mixture was further heated at 95—100 °C for 2 h. After cooling, the mixture was filtered and the collected solid was

Table 2. ^{1}H NMR Data and Redox Potentials of Products **4—11**

Compound	δ-Value[a] Ar-H	δ-Value[a] Bridge-CH_2	$E^1_{1/2}$/V[b]	$E^2_{1/2}$/V[b]
4	9.06	3.19	−0.59	−1.03
5	9.29	3.23	−0.61	−1.05
6	9.21	3.21	−0.63	−1.08
7	9.30	3.23	−0.72	−1.17
8	9.69	3.38	−0.70	−1.15
9	9.50	3.20	−0.62	−1.07
10	9.31	3.20	−0.51	−0.92
11	9.35	3.48	—	—
MV^{2+}	—	—	−0.53	−0.90

a) 60 MHz in DMSO-d_6. b) Volts vs. saturated calomel electrode at a glassy carbon electrode and the counter electrode was a Pt wire; 0.1 M Et_4NClO_4–DMF, scan rate 0.1 V s^{-1}.

recrystallized from benzene–ethanol (2:1) to give 203 mg (yield: 87%) of **5** as pale yellow fine crystals; mp 282—285 °C (decomp). UV (CH_3OH) 300 nm (log ε=4.29). ^1H NMR (DMSO-d_6) δ=1.63 (6H, t, J=7 Hz, CH_3), 3.23 (8H, s, benzylic CH_2), 4.69 (4H, q, J=7 Hz, N^+–CH_2), 9.23 (4H, s, aromatic H). Found: C, 50.75; H, 5.30; N, 6.59%; Calcd for $C_{18}H_{22}N_2Br_2$: C, 50.73; H, 5.20; N, 6.57%.

The other 2,7-disubstituted 4,5,9,10-tetrahydro-2,7-diazoniapyrene salts were prepared in a similar way to that used for **5** under the conditions as shown in Table 1.

2,7-Dipropyl-4,5,9,10-tetrahydro-2,7-diazoniapyrene Dibromide (6): Pale yellow fine crystals from benzene–ethanol (yield: 87%), mp 270—280 °C (decomp). UV (CH_3OH) 313 nm (log ε=4.49). ^1H NMR (DMSO-d_6) δ=0.95 (6H, t, J=7 Hz, CH_3), 2.05 (4H, sext, J=7 Hz, CH_2 in propyl), 3.21 (8H, br. s, benzylic CH_2), 4.60 (4H, t, J=7 Hz, N–CH_2), 9.21 (4H, s, aromatic H). Found: C, 52.85; H, 5.75; N, 6.24%; Calcd for $C_{20}H_{26}N_2Br_2$: C, 52.88; H, 5.77; N, 6.17%.

2,7-Diisopropyl-4,5,9,10-tetrahydro-2,7-diazoniapyrene Dibromide (7): Pale yellow columns from ethanol (yield: 68%), mp 270—275 °C (decomp). UV (CH_3OH) 300 nm (log ε=4.28). ^1H NMR (DMSO-d_6) δ=1.69 (6H, d, J=7 Hz, CH_3), 3.23 (8H, s, benzylic H). 5.07 (2H, hept, J=7 Hz, N–CH), 9.30 (4H, s, aromatic H). Found: C, 52.12; H, 5.62; N, 6.19%; Calcd for $C_{20}H_{26}N_2Br_2 \cdot 1/2\ H_2O$: C, 51.85; H, 5,89; N, 6.05%.

2,7-Dioctadecyl-4,5,9,10-tetrahydro-2,7-diazoniapyrene Dibromide (8): Pale yellow fine crystals from acetone–chloroform (yield: 91%), mp 261—268 °C (decomp). UV (CH_3OH) 301 nm (log ε=4.31). ^1H NMR (DMSO-d_6) δ=0.7—2.9 (66H, m, CH_3 and CH_2 in stearyl except N–CH_2), 3.38 (8H, br. s, benzylic H), 4.6—5.1 (4H, m, N–CH_2), 9.69 (4H, br. s, aromatic H). Found: C, 65.41; H, 9.54; N, 3.05%; Calcd for $C_{50}H_{86}N_2Br_2 \cdot 1/2H_2O$; C, 65.91; H, 9.97; N, 3.07%.

2,7-Dibenzyl-4,5,9,10-tetrahydro-2,7-diazoniapyrene Dichloride (9): Pale yellow fine crystals from benzene–ethanol (yield: quant.), mp 195—200 °C (decomp). UV (CH_3OH) 302 nm (log ε=4.28). ^1H NMR (DMSO-d_6) δ=3.20 (8H, s, bridge CH_2), 5.92 (4H, s, N–CH_2), 7.3—7.8 (10H, m, Aromatic H of benzene), 9.50 (4H, s, aromatic H of pyridine). Found: C, 72.12; H, 5.89; N, 5.94%; Calcd for $C_{28}H_{26}N_2Cl_2 \cdot 1/4H_2O$: C, 72.17; H, 5.74; N, 6.01%.

2,7-Bis(4-cyanobenzyl)-4,5,9,10-tetrahydro-2,7-diazoniapyrene Dibromide (10): Yellow needles from methanol (yield: 53%), mp 194—196 °C (decomp). UV (CH_3OH) 303 nm (log ε=4.30). IR(Nujol) 2240 cm^{-1} (ν_{CN}). ^1H NMR (DMSO-d_6) δ=3.20 (8H, br. s, bridge CH_2), 6.00 (4H, br. s, N–CH_2), 7.82 and 7.96 (8H, AA'BB', J_{AB}=8 Hz, aromatic H of benzene), 9.31 (4H, s, aromatic H of pyridine). Found: C, 59.33; H, 4.08; N, 9.25%; Calcd for $C_{30}H_{24}N_4Br_2 \cdot 1/2H_2O$: C, 59.13; H, 4.14; N, 9.15%.

2,7-Bis(2,4-dinitrophenyl)-4,5,9,10-tetrahydro-2,7-diazoniapyrene Dichloride (11): A mixture of 500 mg (1.33 mmol) of **4**, 3.90 g (19.2 mmol) of 1-chloro-2,4-dinitrobenzene, and methanol (2.5 ml) was refluxed with magnetic stirring for 12.5 h under a nitrogen atmosphere. After cooling, the mixture was evaporated. To the oily residue, some benzene was added. A resulting solid was collected and recrystallized from methanol to give 1.24 g (yield: 84%) of **11** as yellow prisms; mp 156—164 °C (decomp). UV (CH_3OH) 313 nm (log ε=4.49). IR(Nujol) 1550 and 1345 cm^{-1} (ν_{NO_2}). ^1H NMR (DMSO-d_6) δ=3.48 (8H, s, Ha), 8.43 (2H, d, J=8 Hz, He), 8.95 (2H, dd, J=2 and 8 Hz, Hd), 9.29 (2H, d, J=2 Hz, Hc), 9.35 (4H, s, Hb). Found: C, 50.15, H, 3.10; N, 13.46%; Calcd for $C_{26}H_{18}N_6O_8Cl_2 \cdot 1/2H_2O$: C, 50.17; H, 3.08; N, 13.50%.

7-(2,4-Dinitrophenyl)-4,5,9,10-tetrahydro-2-aza-7-diazoniapyrene Chloride (12): A mixture of 200 mg (0.96 mmol) of **4**, 1.556 g (7.68 mmol) of 1-chloro-2,4-dinitrobenzene, and methanol (1 ml) was heated at 50—55 °C with magnetic stirring for 7 h under a nitrogen atmosphere. After cooling, the mixture was evaporated up to give an oily residue and acetone was added.

Recrystallization of the resulting solid from benzene–ethanol gave 238 mg (yield: 60%) of **12** as a pale yellow powder, mp 165—170 °C (decomp). ^1H NMR (CH_3OH-d_4) δ=3.48 (8H, br. s, bridge CH_2), 8.34 (1H, d, J=8 Hz, He), 8.64 (2H, br. s, aromatic H of pyridine), 8.92 (1H, dd, J=2 and 8 Hz, Hd), 9.14 (2H, s, aromatic H of pyridinium ring), 9.26 (1H, d, J=2 Hz, Hc). Found: C, 57.36; H, 3.79; N, 13.16%; Calcd for $C_{20}H_{15}N_4O_4Cl \cdot 1/2H_2O$: C, 57.21; H, 3.84; N, 13.34%.

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References

1) The Chemistry of Constrained Hetero Aromatics. IV.
2) C. L. Bird and A. T. Kuhn, *Chem. Soc. Rev.*, **10**, 49 (1981).
3) T. Kawashima, K. Yoshida, Y. Tohda, M. Ariga, Y. Mori, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, **25**, 1585 (1984).
4) T. Kawashima, Y. Ishizaki, Y. Tohda, M. Ariga, Y. Mori, and S. Misumi, *Mem. Osaka Kyoiku Univ.*, **35**, 139 (1986).
5) Extensive references therein: K. Nishiyama, K. Hata, and T. Sato, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 557.
6) The conditions applied for dimerization of pyridine were modified; A. T. Nielsen, *J. Org. Chem.*, **29**, 2175 (1964).
7) J. G. Allen, UK Patent 1514466 (1978).