Chiral Recognition in Disproportionation of Monoradical Cation of Optically Active Bisviologen in an Aqueous Solution

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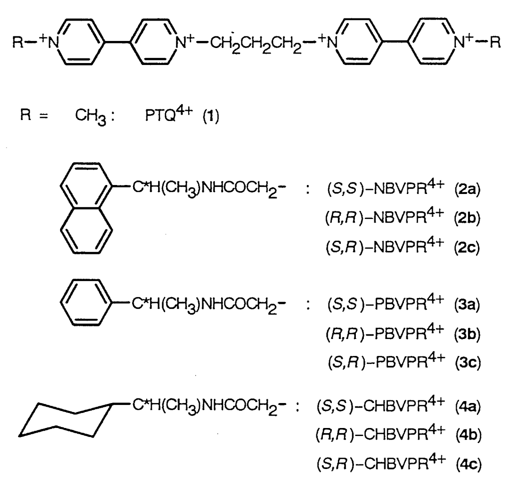
Optically active bisviologens, containing 1-(1-naphthyl)-, 1-phenyl-, and 1-cyclohexylethylamine, were synthesized. Disproportionation of monoradical trications produced by one-electron reduction occurred more easily in the (*S*,*R*)-isomers than in the (*S*,*S*)- and (*R*,*R*)-ones. The disproportionation is controlled by steric bulk of the chiral substituents in *intra*molecular association between two viologen radical units of diradical dications.

Viologens are diquaternary salts of 4,4'-bipyridine and have been used as electron acceptors in a great variety of studies in such areas as biochemical redox systems, herbicidal activity, electrochemistry, photochemistry, and solar energy conversion.[1] Bisviologens, 1,1''-poly(methylene)bis(1'-methyl-4,4'-bipyridinium) ions, are tetraquaternary salts which contain two viologen units, joined by a varying number of methylene groups.[2-4] One-electron reduced monoradical trication, especially trimethylene bridged $\mathrm{PTQ}^{3+\bullet}$, undergoes disproportionation easily to the diradical dication ($\mathrm{PTQ}^{2+\bullet\bullet}$) and the parent bisviologen (PTQ^{4+}, **1**) in solution.[3,4] It has been suggested that the doubly reduced $\mathrm{PTQ}^{2+\bullet\bullet}$ adopts an *intra*molecular associated form ("closed" conformation) and the disproportionation is mainly controlled by the comproportionation rate constant.[4] We have recently reported optically active viologens, containing 1-(1-naphthyl)-, 1-phenyl-, and 1-cyclohexylethylamine.[5] In continuation of our interest in chiral viologens, we have synthesized optically active bisviologens (**2**—**4**) and found chiral recognition in disproportionation of the monoradical trication of these bisviologens.



The (*S*,*S*)- and (*R*,*R*)-isomers of optically active bisviologens were prepared by the reaction of 1,1''-trimethylenebis(4-(4-pyridyl)pyridinium) dibromide[2] with five-fold excess of chiral 1-(1-naphthyl)-, 1-phenyl-, or (1-cyclohexylethyl)carbamoylbromomethane (**5**)[5] in *N*,*N*-dimethylformamide (DMF) at 85 °C for 28 h under nitrogen. Crude products were recrystallized from warm water (yield 12—44%).[6] The (*S*,*R*)-isomer (**3c**) was prepared by the following way under the reaction conditions at 85 °C for 28 h in DMF under nitrogen. (*S*)-1-(1-Phenylethyl)carbamoylmethyl-4-(4-pyridyl)pyridinium bromide (**6**, yield 40%), which was obtained by the reaction of the (*S*)-isomer of **5** with large excess of 4,4'-bipyridine, was treated with 1,3-dibromopropane. The resulted (*S*)-1-(1-phenylethyl)carbamoylmethyl-1'-(3-bromopropyl)-4,4'-bipyridinium dibromide (**7**, yield 85%) was reacted with 4,4'-bipyridine in large excess to give (*S*)-1-(1-phenylethyl)carbamoylmethyl-1'-(4-(4-pyridyl)pyridinio)propyl-4,4'-bipyridinium tribromide (**8**, yield 48%). The compound **8** was further treated with (*R*)-isomer of **5** in large excess to give the desired compound (yield 68%). The compounds **2c** and **4c** were also prepared by the same method as described above. Crude products were recrystallized from warm water.[6] Bromides were converted to chloride salts by an anion exchange chromatography for spectroscopic measurements. Disproportionation constants of the monoradical trications were determined spectrophotometrically by the same method described in the literature,[4] where sodium

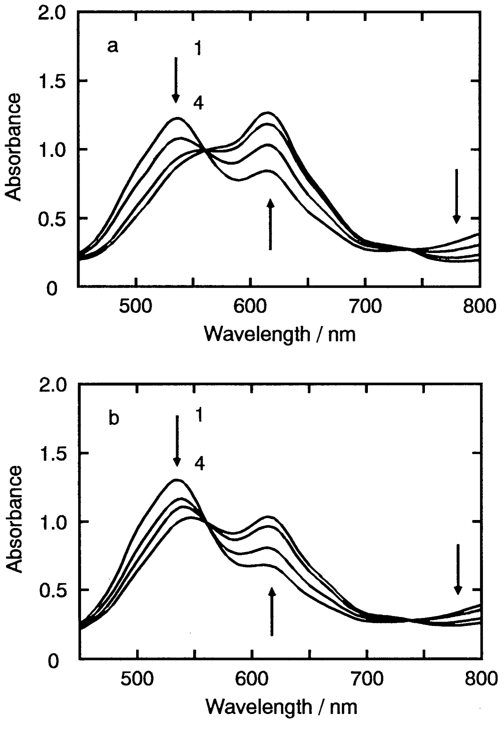


Figure 1. Absorption spectral changes for the equilibrium between $\mathrm{NBVPR}^{3+\bullet}$ and $\mathrm{NBVPR}^{2+\bullet\bullet}$ in the presence of NBVPR^{4+} in excess at 25 °C, pH 7.0 (0.01 mol dm^{-3} phosphate buffer), and I = 0.04 mol dm^{-3} (NaCl). Total concentrations of radicals are 1.30×10^{-4} mol dm^{-3}. (a) Total concentrations of (*R*,*R*)-isomer / mol dm^{-3} = 3.40×10^{-4} (1), 6.80×10^{-4} (2), 1.36×10^{-3} (3), and 2.04×10^{-3} (4). (b) Total concentrations of (*S*,*R*)-isomer / mol dm^{-3} = 5.00×10^{-4} (1), 1.00×10^{-3} (2), 2.00×10^{-3} (3), and 3.00×10^{-3} (4).

Table 1. Disproportionation constants and redox potentials of bisviologens at 25 °C, pH 7.0, and $I = 0.04$ mol dm^{-3}

Bisviologen	K_{disp}	Ratio	$E_1^{0\ a,b}$/V	$E_2^{0\ a,c}$/V
2				
(S,S)- & (R,R)-	2.5±0.4		-0.18_2	-0.15_8
(S,R)-	10.0±3.0	4.0	-0.20_0	-0.14_0
3				
(S,S)- & (R,R)-	4.6±1.3		-0.23_0	-0.19_0
(S,R)-	7.4±2.0	1.6	-0.23_6	-0.18_4
4				
(S,S)- & (R,R)-	9.9±3.4		-0.23_9	-0.18_4
(S,R)-	18.0±4.0	1.8	-0.24_7	-0.17_3
1[d]	260±60		-0.33	-0.19

[a] Determined from the two-electron redox potentials (vs NHE) by a cyclic voltammetry and the disproportionation constants. Errors are ±0.005 V. [b] For the couple of the parent bisviologen/monoradical trication. [c] For the couple of monoradical trication/diradical dication. [d] Reference 4.

dithionite (Fluka) was used as a reducing agent.

Figure 1 shows spectral changes for the equilibrium between $NBVPR^{3+\cdot}$ and $NBVPR^{2+\cdot\cdot}$ (Eq. 1) in the presence of large excess of $NBVPR^{4+}$ at the constant total concentrations of radicals.

$$2NBVPR^{3+\cdot} \rightleftharpoons NBVPR^{2+\cdot\cdot} + NBVPR^{4+} \qquad (1)$$

When the concentrations of $NBVPR^{4+}$ increased, the absorption at 615 nm (λ_{max} of $NBVPR^{3+\cdot}$) increased with concurrent decreasing in absorption at 532 nm (λ_{max} of $NBVPR^{2+\cdot\cdot}$) with isosbestic points at 560 nm and 740 nm. The spectral change for the (R,R)-isomer is larger than that for the (S,R)-one, indicating that the disproportionation of $NBVPR^{3+\cdot}$ occurs more easily in the latter than in the former. The disproportionation constants (K_{disp}) were determined at both 532 nm and 615 nm at a variety of total concentrations of radicals (5.3×10^{-5} — 1.7×10^{-4} mol dm^{-3}).[7] The values of K_{disp} are listed in Table 1 along with those of the redox potentials. K_{disp} values of (S,S)- and (R,R)-isomers are identical and smaller than those of (S,R)-isomers for all of the chiral bisviologens. Ratios of K_{disp} of the (S,R)-isomer to that of the (S,S)- or (R,R)-isomer are 4.0 (naphthyl) > 1.8 (cyclohexyl) ≥ 1.6 (phenyl), whose tendency is in response to steric bulk of the chiral substituents. It has been suggested that the diradical dication adopts a "closed" conformation where each viologen radical-cation unit interacts intramolecularly.[4,8] Therefore, the absorption maximum shifts to 532 nm from 610 nm that is expected to an "open" form.[4] Kinetic studies have demonstrated that the disproportionation is mainly controlled by the comproportionation rate constant which is smaller for stronger interactions in the closed conformation.[4] Chiral recognition in disproportionation may arise from the difference in steric repulsion between chiral substituents in the closed form of the diradical dication. The (S,R)-isomer can adopt a mirror-image conformation in such an *intra*molecular association and the steric repulsion decreases in contrast to (S,S)- and (R,R)-isomers; therefore, the disproportionation occurs easily in the former. In contrast, a relatively small methyl subsituent of $PTQ^{3+\cdot}$ facilitates the disproportionation.

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6 **2**: ^{1}H NMR (270 MHz, D_2O, DSS) δ=9.18 (4H, d, J=6.8 Hz, 2',6'-bpy), 8.99 (4H, d, J=6.8 Hz, 2,6-bpy), 8.57 (4H, d, J=7.3 Hz, 3',5'-bpy), 8.54 (4H, d, J=6.8 Hz, 3,5-bpy), 8.12 (2H, d, J=8.1 Hz, 8-naphthyl), 7.98 (2H, d, J=8.3 Hz, 5-naphthyl), 7.90 (2H, d, J=7.8 Hz, 4-naphthyl), 7.64 (2H, d, J=5.9 Hz, 2-naphthyl), 7.53 — 7.62 (6H, m, 3,6,7-naphthyl), 5.78 (2H, q, J=7.5 Hz, CH), 5.58 — 5.62 (4H, m, $COCH_2$-$^+$N), 4.94 (4H, *t*, J=7.6 Hz, α-CH_2), 2.84—2.96 (2H, m, β-CH_2), 1.66 (6H, d, J= 6.8 Hz, CH_3). UV-vis (H_2O, λ_{max}/nm (logε)) 260sh (4.76), 270 (4.78), 280sh (4.73). ORD (*c* 0.050, H_2O, 20 °C) $[\Phi]_{589}$ -60° for **2a**, 61° for **2b**, 0° for **2c**. Found: C, 52.04; H, 4.63; N, 7.23%. Calcd for (S,S)-$C_{51}H_{50}N_6O_2Br_4 \cdot 4.5H_2O$ (**2a**): C, 51.93; H, 5.04; N, 7.12%. Found: C, 51.70; H, 4.86; N, 7.16%. Calcd for (R,R)-$C_{51}H_{50}N_6O_2Br_4 \cdot 4.5H_2O$ (**2b**): C, 51.93; H, 5.04; N, 7.12%. Found: C, 51.01; H, 4.54; N, 7.25%. Calcd for (S,R)-$C_{51}H_{50}N_6O_2Br_4 \cdot 5H_2O$ (**2c**): C, 51.53; H, 5.09; N, 7.07%. **3**: ^{1}H NMR (270 MHz, D_2O, DSS) δ=9.19 (4H, d, J=6.8 Hz, 2',6'-bpy), 9.00 (4H, d, J=6.8 Hz, 2,6-bpy), 8.59 (4H, d, J=7.3 Hz, 3',5'-bpy), 8.55 (4H, d, J = 7.3 Hz, 3,5-bpy), 7.30 — 7.45 (10H, m, phenyl), 5.53—5.67 (4H, m, $COCH_2$-$^+$N), 4.96 (2H, q, J=7.4 Hz, CH), 4.95 (4H, *t*, J=7.5 Hz, α-CH_2), 2.86—2.97 (2H, m, β-CH_2), 1.50 (6H, d, J=6.8 Hz, CH_3). UV-vis (H_2O, λ_{max}/nm (logε)) 265 (4.83). ORD (*c* 0.050, H_2O, 20 °C) $[\Phi]_{589}$ -144° for **3a**, 145° for **3b**, 0° for **3c**. Found: C, 49.63; H, 4.68; N, 8.02%. Calcd for (S,S)-$C_{43}H_{46}N_6O_2Br_4 \cdot 2H_2O$ (**3a**): C, 49.92; H, 4.87; N, 8.12%. Found: C, 50,06; H, 4.57; N, 8.15%. Calcd for (R,R)-$C_{43}H_{46}N_6O_2Br_4 \cdot 2H_2O$ (**3b**): C, 49.92; H, 4.87; N, 8.12%. Found: C, 48.79; H, 4.68; N, 7.90%. Calcd for (S,R)-$C_{43}H_{46}N_6O_2Br_4 \cdot 3H_2O$ (**3c**): C, 49.07; H, 4.98; N, 7.98%. **4**: ^{1}H NMR (270 MHz, D_2O, DSS) δ=9.21 (4H, d, J=5.4 Hz, 2',6'-bpy), 9.04 (4H, d, J=5.4 Hz, 2,6-bpy), 8.61 (4H, d, J=5.6 Hz, 3',5'-bpy), 8.59 (4H, d, J= 5.6 Hz, 3,5-bpy), 5.53—5.58 (4H, m, $COCH_2$-$^+$N), 4.97 (4H, t, J=7.3 Hz, α-CH_2), 3.68 — 3.77 (2H, m, CH), 2.88 — 2.98 (2H, m, β-CH_2), 1.60 — 1.76 (12H, m, cyclohexyl), 1.32 — 1.43 (2H, m, cyclohexyl), 1.08—1.27 (4H, m, cyclohexyl), 1.13 (6H, d, J=6.8 Hz, CH_3), 0.90 — 1.03 (4H, m, cyclohexyl). UV-vis (H_2O, λ_{max} / nm (logε)) 265 (4.70). ORD (*c* 0.050, H_2O, 20 °C) $[\Phi]_{589}$ -43° for **4a**, 43° for **4b**, 0° for **4c**. Found: C, 47.78; H, 6.08; N, 7.80%. Calcd for (S,S)-$C_{43}H_{58}N_6O_2Br_4 \cdot 4H_2O$ (**4a**): C, 47.71; H, 6.14; N, 7.76%. Found: C, 48.39; H, 5.91; N, 7.74%. Calcd for (R,R)-$C_{43}H_{58}N_6O_2Br_4 \cdot 3H_2O$ (**4b**): C, 48.51; H, 6.06; N, 7.89%. Found: C, 48.79; H, 5.69; N, 7.65%. Calcd for (S,R)-$C_{43}H_{58}N_6O_2Br_4 \cdot 3H_2O$ (**4c**): C, 48.51; H, 6.06; N, 7.89%.

7 Molar absorption coefficients used for calculation of K_{disp} at 532 nm and 615 nm for each bisviologen species are as follows: ε_{532}/dm^3 mol^{-1} cm^{-1} 2.81×10^4 ($NBVPR^{2+\cdot\cdot}$), 4.96×10^3 ($NBVPR^{3+\cdot}$), 3.36×10^4 ($PBVPR^{2+\cdot\cdot}$), 5.60×10^3 ($PBVPR^{3+\cdot}$), 2.74×10^4 ($CHBVPR^{2+\cdot\cdot}$), 4.34×10^3 ($CHBVPR^{3+\cdot}$); ε_{615}/dm^3 mol^{-1} cm^{-1} 4.59×10^3 ($NBVPR^{2+\cdot\cdot}$), 1.30×10^4 ($NBVPR^{3+\cdot}$), 4.40×10^3 ($PBVPR^{2+\cdot\cdot}$), 1.47×10^4 ($PBVPR^{3+\cdot}$), 3.44×10^3 ($CHBVPR^{2+\cdot\cdot}$), 1.14×10^4 ($CHBVPR^{3+\cdot}$).

8 Since the value of K_{disp} for a 1:1 mixture of (S,S)- and (R,R)-$NBVPR^{4+}$ was in agreement with that for the (S,S)- and (R,R)-isomers, *inter*molecular interaction between viologen radical units in the diradical dication might be negligible.