Synthesis of Photochromic Benzodixanthene Analogues with 2-Pyridyl Group and Formation of Monolayers on Water Surface

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Nitrogen analogues of benzo[1, 2, 3-*kl* : 4, 5, 6-*k'l'*]dixanathene with 2-pyridyl group were synthesized from 1,5-dichloroanthraquinone in six steps. After quaternization with iodoalkane, photochromic properties were investigated in ethanol or in toluene. The compound having a decyl group formed monolayer on water surface at 10 °C.

Keywords: benzodixanthene, quaternization, photochromism, monolayer

1. Introduction

Benzo[1, 2, 3-*kl* : 4, 5, 6-*k'l'*]dixanthene (**1a**) and its analogues are well known as typical polycondensed aromatic compounds having photochromic properties.[1] Molecular design of analogues of **1a** and its isomer **3a** were performed to predict absorption maxima of these compounds.[2] The relation between the coefficients of highest occupied molecular orbitals of **1a** or **3a** and the conformation of their endoperoxide was investigated by semi-empirical molecular orbital method and X-ray crystallographic analysis.[3]

Photochromic properties of monolayers on water surface have been widely studied. Mixtures of the alkylsubstituted thioindigo dyes and tripalmitine were found to form monomolecular films and to control the photochromic reaction in the Langmuir - Blodgett films.[4] The Langmuir - Blodgett films of spiropyran derivatives have been extensively studied.[5] Seki *et al.* have reported the photochemical behavior of poly(vinyl alcohol)s having an azobenzene side chain and azobenzene mono-

layers.[6] The rates and the surface pressure dependence of the photochromic reaction of spirobenzoselenazopyrans with long chains in monolayers on water surface has been investigated.[7]

However, any derivative of **1a** or **3a** has not been reported to construct monolayers on water surface. In the present work, we synthesized several novel photochromic compounds (**1c** - **1g**) containing 2-pyridyl group. The solubilities and the photochromic properties of these compounds were studied. Furthermore, the monolayers spread from their benzene solution were preliminarily examined.

2. Method

Solvents and reagents were purified using literature method. Thin-layer chromatography (TLC) was performed on plastic or glass plate (10 x 5 cm) coated with Merck 5735 silica gel 60F. Column chromatography was performed using Wakogel C-300 (200-300 mesh, Wako Pure Chemical Industries, Ltd.). Melting points were determined with a Büch melting point

apparatus and were uncorrected. UV-VIS spectra were recorded on a Shimadzu UV-2100 spectrophotometer. IR spectra were obtained on JASCO A-302 and Perkin-Elmer 1600 FT-IR. ^1H NMR spectra were recorded on Bruker AM-400 spectrometer, using tetramethylsilane as an internal standard.

2.1 Synthetic routes

Synthetic routes to compounds **1c** - **1g** are shown in Scheme 1.

2.2 Computational method

Geometries are initially optimized by molecular mechanics [9] with CAChe.[10] After further optimization by AM1 procedure [11] absorption maxima were calculated using INDO/S.[12]

2.3 Formation of monolayers on water surface

Monolayers were spread from the benzene solution on the distilled water surface and the surface pressure - area (π - A) isotherms were measured by using a Lauda film balance.

3. Results and Discussion

3.1 Absorption maxima

The electronic spectrum of **1b** showed a bathochromic shift compared with that of **1a**. [2] The introduction of more electron-donating atom -N< instead of -O- was explained to cause a

Scheme 1

bathochromic shift. [8]

The absorption maximum of **1c** shifted to slightly shorter wavelength than that of **1b**. The electron-withdrawing effect of 2-pyridyl group in **1c** weakens the electron-donating effect of the nitrogen atom -N< of **1b** to give hypsochromic shift.

The absorption maxima of quaternary compounds **1d** - **1g** shifted to shorter wavelengths than those of **1b** - **1c**. These tendencies indicate that the electron-withdrawing effect of the cation $=\text{N}^+<$ is much stronger than that of the nitrogen atom -N= of 2-pyridyl group.

Table 1. First absorption maxima of **1a** and its analogues

	$\lambda_{\text{max, obs}}/\text{nm}$		$\lambda_{\text{max, calc}}/\text{nm}$
	toluene	ethanol	
1a	541		462
1b	589		483
1c	582	574	482
1d		547	472
1e		546	471
1f	558	546	472
1g	557	540	470

The correlation between calculated and observed wavelengths of **1a** - **1g** is shown in Fig. 1. The calculated wavelengths are shorter than observed ones, however, the correlation between

them may be reasonable, judging from the fittings of correlation lines. In many cases, absorption maxima calculated by ZINDO approximation have tendency to give similar results.[13]

Fig. 1 Correlation between calculated wavelengths (in vacuum) and observed ones (in toluene or in ethanol).

3.2 ^1H NMR

A ^1H NMR analysis of benzodioxanthene analogues gave a similar explanation to the above discussion (§ 3.1) concerning the electron-donating properties of nitrogen atom in the molecular framework.

The signal of H_l in **1b** appears upfield from those of bay protons such as phenanthrenes or benzophenanthrenes. Similarly, the signal of H_c in **1b** appears upfield from those of ordinary aromatic protons reflecting the electron-donating effect of nitrogen atom $-\text{N}<$.

The chemical shifts of H_a and H_n are observed at the higher field than H_l or H_c depending on the electron-donating effect of the nitrogen atom $-\text{N}<$ of the molecular framework together with the shielding effect of aryl (phenyl or pyridyl) group which lies almost perpendicular to the average plane of mother structure (benzodioxanthene analogue).

Reflecting the perpendicular geometry of phenyl (or pyridyl) ring to the mother structure, the ^1H NMR signals of **1c** are similar to those of **1b**. On the other hand, the chemical shifts of **1f** (or **1g**) are observed at lower field than those of **1b** or **1c**. These results may be ascribed to the stronger electron-withdrawing ability of $=\text{N}^+<$ than that of $-\text{N}=$ in 2-pyridyl group.

To say a long story short, the observed electron-withdrawing effect of 2-pyridyl group is small, however, that of quaternary atom is large in ^1H NMR, coincided with the observed tendencies in UV-VIS spectra.

Table 2. ^1H NMR chemical shifts (δ/ppm)

	Z	H_l	H_c	H_a	H_n
1b	CH	7.80	7.04	6.28	5.78
1c	N	7.82	7.08	6.17	5.72
1f	$^+\text{N}-\text{C}_8\text{H}_{17}$	8.19	7.29	6.45	5.99
1g	$^+\text{N}-\text{C}_{10}\text{H}_{21}$	8.17	7.27	6.44	6.00

Scheme 2

3.3 Photochromic properties

Spectral changes accompanied with the photooxidation reaction of **1c** in toluene under irradiation of 582 nm light are shown in Fig. 2. The peak heights of absorption maxima at 582 nm, 546 nm, and 424 nm of **1c** are decreased, and the peak height at 340 nm (ascribed to endoperoxide **2c**) is increased.

Fig. 2. Spectral changes of **1c** in toluene under photooxidation

The endoperoxide **2c** regenerated **1c** upon heating at 110 °C. Analogous compounds **1d** - **1g** showed similar spectral changes with irradiation of visible light in toluene solutions.

3.4 Solvent effect

1a and **1b** were not soluble in polar solvent. On the other hand, **1d** and **1e** were soluble in water or ethanol. In ethanol, photooxidation of **1d** or **1e** occurred to give its endoperoxide **2d** or **2e**, respectively. Heating the ethanol solution of endoperoxide over 78 °C regenerated **1d** or **1e**. In water, however, the similar photochromic reactions of **1d** or **1e** were not observed.

1f and **1g** were soluble in ethanol or toluene. The photochromic reactions were observed in these solvent.

Absorption maxima of **1f** (or **1g**) in ethanol shifted to shorter wavelengths than those in toluene, respectively. As the polarization around $-N^+$ may be more facilitated in water than in ethanol, the 2-pyridinium group in water will withdraw the electron move strongly than in ethanol.

3.5 Monolayers on water surface

We have investigated the possibility of monolayer formations of **1f** and **1g** on the water surface. The surface pressure - area (π - A) isotherms for the monolayers of each compound under the dark condition are shown in Fig. 3. The photochromic compound **1g** with decyl chain at 10 °C forms the condensed monolayer with a limiting area of 30 Å²/molecule. In this case, it is considered that π -electron systems of the molecular frameworks of **1g** stand side by side.

Fig. 3. Surface pressure - area isotherms of **1f** and **1g** under dark condition.

The C-N bond between nitrogen atom of the molecular framework and carbon atom of 2-pyridyl group is fairly free rotation, therefore the alkyl chain will be nearly perpendicular to the water surface.

4. Experimental

1-amino-5-chloroanthraquinone (5).

Compound **5** was prepared as described in the reference.[14] Red needles (from acetone) in 17 % yield, mp 198-210 °C; IR(cm⁻¹ /KBr) 3428, 3320, 1628, 1555 and 1271; ¹H NMR (CDCl₃/TMS, δ ppm) 6.82 (br, 2H, NH), 6.96 (dd, 1H), 7.48 (t, 1H), 7.58-7.67 (m, 2H), 7.74 (dd, 1H) and 8.31 (dd, 1H); UV-VIS (nm in ethanol) 478 and 312.

1-amino-5-phenoxyanthraquinone (6).

A mixture of 1-amino-5-chloroanthraquinone **5** (1.00 g, 3.87 mmol), potassium phenoxide (3.00 g, 20.3 mmol), pyridine (12 ml) was heated under reflux at 105 °C for 4h under argon atmosphere. The product was extracted with chloroform, pyridine was removed by 1% hydrochloric acid. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (toluene /silica gel). Recrystallization from toluene afforded **6** (546 mg, 1.72 mmol, 45 %). Red needles, mp 197-200 °C; IR(cm⁻¹ /KBr) 3428, 1663, 1614 and 1272; ¹H NMR (CDCl₃/TMS, δ ppm) 6.82 (br, 2H, NH), 6.93 (dd, 1H), 7.04 (dd, 2H), 7.11-7.25 (m, 2H), 7.34-7.46 (m, 2H), 7.44 (t, 1H), 7.56 (dd, 1H), 7.65 (t, 1H) and 8.13 (dd, 1H); UV-VIS (nm in ethanol) 480.

1-anilino-5-phenoxyanthraquinone (7).

A mixture of **6** (1.00 g, 3.15 mmol), iodobenzene (700 mg, 3.43 mmol), copper powder (240 mg, 3.78 mmol), anhydrous potassium carbonate (407 mg, 4.10 mmol), and bromobenzene (25 ml) was heated under reflux at 145 °C for 7 h under argon atmosphere. Bromobenzene and iodobenzene were removed by steam distillation, the copper was filtered with chloroform under heating. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (toluene/silica gel). Recrystallization from toluene afforded **7** (1.01g, 2.27 mmol, 88 %). Purple needles, mp 187-189 °C; IR(cm⁻¹ /KBr) 3467, 1594, 1516 and 1272; ¹H NMR (CDCl₃/TMS, δ ppm) 7.06

(dd, 1H), 7.13-7.21 (m, 2H), 7.31-7.49 (m, 10H), 7.58-7.71 (m, 2H), 8.16 (dd, 1H) and 11.27 (s, 1H, NH); UV-VIS (nm in ethanol) 503.

1-(1-phenyl-2-bipyridylamino)-5-phenoxyanthraquinone (8). A mixture of **7** (500 mg, 1.28 mmol), 2-bromopyridine (11.0 g, 69.7 mmol), copper powder (300 mg, 4.72 mmol), hydrous potassium carbonate (300 mg, 3.03 mmol) was heated under reflux at 160 °C for 4 h under argon atmosphere. 2-bromopyridine was removed by steam distillation. After drying, the copper was filtered with chloroform during heating. The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (toluene-ethyl acetate (10 : 1)/silica gel). Recrystallization from methanol afforded **8** (369 mg, 0.79 mmol, 62%). Purple needles, mp 160-163 °C; IR(cm^{-1} /KBr) 3457, 2934, 1682 and 1278; ^1H NMR (CDCl_3/TMS , δ ppm) 6.70 (d, 1H), 6.97 (dd, 2H), 7.02-7.15 (m, 3H), 7.20-7.28 (m, 5H), 7.31-7.34 (m, 1H), 7.35-7.43 (m, 3H), 7.53-7.62 (m, 2H), 7.91 (dd, 1H) and 8.04 (dd, 1H); UV-VIS (nm in ethanol) 494, 350 and 252.

xantheno[1', 9' : 4, 5, 6]benzo[1, 2, 3-*kl*]N-(2-pyridyl) acridine (1c). A mixture of **8** (141.5 mg, 0.303 mmol), hydroquinone (140 mg, 1.30 mmol), sodium chloride (200 mg, 3.42 mmol), anhydrous aluminum chloride (2.00 g, 15.0 mmol) was heated under reflux at 160 °C for 1.5 h. After cooling, 2 mol/l hydrochloric acid was added carefully and neutralized by 3 mol/l sodium hydroxide. The resultant was filtered with suction. The residue was washed with a solution of sodium dithionite (4.00 g, 22.0 mmol) and sodium hydroxide (2.00 g, 0.10 mmol) in water (100 ml). After washing, the residue was dried in a desiccator for 24 h. The residue was dissolved in toluene and purified by column chromatography (chloroform/silica gel). Recrystallization from toluene afforded **1c** (39.5 mg, 0.091 mmol, 30 %). Purple needles, mp 259 °C; IR(cm^{-1} /KBr) 2929, 1467 and 1276; ^1H NMR (CDCl_3/TMS , δ ppm) 5.72 (d, 1H), 6.17 (d, 1H), 6.99 (d, 1H), 7.08 (d, 1H), 7.14-7.25 (m, 4H), 7.37 (t, 2H), 7.66-7.73 (m, 2H), 7.82 (d, 1H), 8.03 (d, 1H), 8.12 (d, 1H), 8.19 (d, 1H), 8.28 (dd, 1H) and 8.92 (dd, 1H); UV-VIS (nm in ethanol (log ϵ)) 573 (3.74), 540 (3.70) and 422

(3.31); UV-VIS (nm in toluene (log ϵ)) 583 (4.05), 547 (4.01) and 424 (3.61); UV-VIS (nm in chloroform (log ϵ)) 578 (4.30), 543 (4.26) and 425 (3.87).

xantheno[1', 9' : 4, 5, 6]benzo[1, 2, 3-*kl*]N-(1-methyl-2-pyridyl)acridine iodide (1d). A mixture of **1c** (14.7 mg, 0.034 mmol), iodomethane (5.37 mg, 37.8 mmol), acetonitrile (10 ml) was heated under reflux at 80 °C for 7 h under nitrogen atmosphere. The solvent was removed under reduced pressure. The residue was dissolved in toluene. The resultant were collected by filtration with suction to give 8.9 mg (0.015 mmol, 46%) of **1d**. Purple powder; IR(cm^{-1} /KBr) 2921, 1458 and 1267; ^1H NMR (DMSO, δ ppm) 4.17 (s, 3H, CH_3), 5.93 (d, J = 7.6 Hz, 1H), 6.42 (d, J = 7.9 Hz, 1H), 7.09 (d, J = 7.4 Hz, 1H), 7.21-7.32 (m, 5H), 7.42-7.50 (m, 2H), 8.02 (d, J = 8.7 Hz, 1H), 8.11 (d, J = 8.7 Hz, 1H), 8.18 (d, J = 7.8 Hz, 1H), 8.24 (d, J = 7.4 Hz, 1H), 8.45 (t, J = 6.9 Hz, 1H), 8.59 (d, J = 7.9 Hz, 1H), 9.01 (t, J = 7.9 Hz, 1H); UV-VIS (nm in ethanol); 547, 517 and 413; UV-VIS (nm in water); 550, 521 and 415.

xantheno[1', 9' : 4, 5, 6]benzo[1, 2, 3-*kl*]N-(1-ethyl-2-pyridyl)acridine iodide (1e). A mixture of **1c** (15.5 mg, 0.036 mmol), iodoethane (6.5 mg, 41.7 mmol), acetonitrile (10 ml) was heated under reflux at 80 °C for 7 h under nitrogen atmosphere. The solvent was dissolved in toluene. The resultant were collected by filtration with suction to give 7.69 mg (0.013 mmol, 37%) of **1e**. Purple powder; ^1H NMR (DMSO, δ ppm) 1.36 (t, 3H, CH_3), 4.47 (dd, 2H, CH_2), 5.91 (d, 1H), 6.39 (d, 1H), 7.07 (d, 1H), 7.18-7.32 (m, 5H), 7.40-7.51 (m, 2H), 7.99 (d, 1H), 8.09 (d, 1H), 8.19 (d, 1H), 8.25 (d, 1H), 8.47 (t, 1H), 8.60 (d, 1H), 9.00 (t, 1H) and 9.58 (d, 1H); UV-VIS (nm in ethanol) 573, 543 and 422.

xantheno[1', 9' : 4, 5, 6]benzo[1, 2, 3-*kl*]N-(1-octyl-2-pyridyl)acridine iodide (1f). A mixture of **1c** (17.4 mg, 0.04 mmol), 1-iodooctane (536.5 mg, 2.24 mmol), potassium iodide (26.5 mg, 0.16 mmol), and acetonitrile (15 ml) was heated under reflux at 80 °C for 60 h under argon atmosphere. After cooling, the solvent was evaporated under reduced pressure, the resultant was purified by column chromato-

graphy (chloroform/silica gel and acetone/silica gel). The solvent was evaporated under reduced pressure. Recrystallization from water afford **1f** (6.0mg, 8.90×10^{-3} mmol, 22 %). Black purple powder, mp 132-140 °C (decomp); IR(cm^{-1} /KBr) 2948, 1467 and 1281; MS (FAB) (m/z) 547 ($M^+ - 127$, calcd 674, $I = 127$); ^1H NMR (DMSO/TMS, δ ppm) 0.54-1.24 (m, 11H), 1.54 (m, 4H), 4.41 (t, 2H), 5.99 (d, 1H), 6.45 (d, 1H), 7.09 (d, 1H), 7.23-7.33 (m, 5H), 7.40-7.52 (m, 2H), 8.00-8.20 (m, 4H), 8.50 (t, 1H), 8.72 (d, 1H), 9.06 (t, 1H) and 9.57 (d, 1H); UV-VIS (nm in ethanol (log ϵ)) 546 (4.09), 516 (4.06) and 414 (3.64); UV-VIS (nm in toluene (log ϵ)) 558 (4.28), 524 (4.25) and 417 (3.90).

xantheno[1', 9' : 4, 5, 6]benzo[1, 2, 3-kl]N-(1-decyl-2-pyridyl)acridine iodide (1g). A mixture of **1c** (21.5 mg, 0.05 mmol), 1-iododecane (503.0 mg, 1.85 mmol), potassium iodide (22 mg, 0.13 mmol), and acetonitrile (15 ml) was heated under reflux at 80°C for 60 h under argon atmosphere. After cooling, the solvent was evaporated under reduced pressure. The resultant was purified by column chromatography (chloroform/ silica gel and acetone/silica gel). The solvent was evaporated under reduced pressure. Recrystallization from water afforded **1g** (7.7 mg, 10.9×10^{-3} mmol, 22 %). Black purple powder, mp 125-138 °C (decomp); IR(cm^{-1} /KBr) 2958, 1462 and 1286; MS (FAB) (m/z) 575 ($M^+ - 127$, calcd 702, $I = 127$); ^1H NMR (DMSO/TMS, δ ppm) 0.65-1.23 (m, 11H), 1.68-1.74 (m, 4H), 4.38 (t, 2H), 6.00 (d, 1H), 6.44 (d, 1H), 7.08 (d, 1H), 7.20-7.31 (m, 5H), 7.39-7.50 (m, 2H), 7.98-8.18 (m, 4H), 8.49 (t, 1H), 8.72 (d, 1H), 9.05 (t, 1H) and 9.57 (d, 1H); UV-VIS (nm in ethanol (log ϵ)) 546 (3.66), 516 (3.63) and 414 (3.27); UV-VIS (nm in toluene (log ϵ)) 557 (4.28), 524 (4.25) and 416 (3.91).

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