Synthesis and Photochromism of Photochromic Spiro Compounds Having a Reactive Pendant Group

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The photochromic spiropyrans and spirooxazines having a reactive pendant group, including carboxyl, halide, succinimidyl ester and isothiocyanate, were synthesized. Their photochromic behaviors in solution and solid state were studied.

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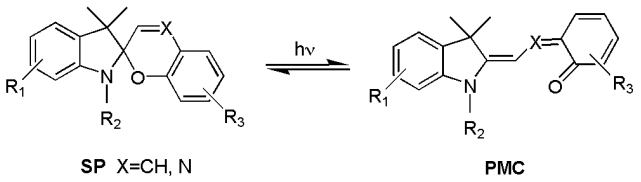
Introduction.

Photochromism involving reversible change in the visible absorption spectrum has attracted much attention in the last decades due to the various potential application of the photochromic system [1,2]. Spiropyrans and spirooxazines, the important classes of photochromic materials, have been extensively investigated [3,4]. The photochromic processes of these compounds are based on intramolecular pericyclic reactions [1] (Scheme 1).

Scheme 1



The reversible transformation between the closed spiro form (SP) and the open photo-merocyanine form (PMC) results in a color change.

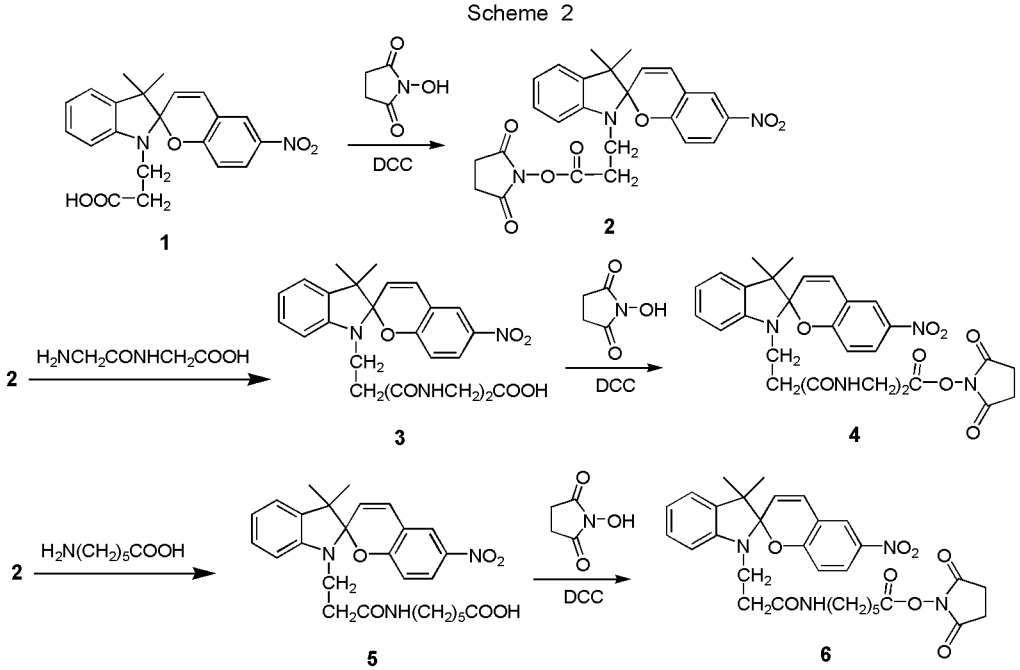
The chemistry of photochromic spiro compounds has been studied with regard to industrial applications and biomolecules modification as photoresponsive materials [5-8]. It is necessary to synthesize the spiro compounds having a reactive pendant group that may be used for biomolecules modification. Some groups, such as carboxyl, halide, succinimidyl ester and isothiocyanate, are suitable for biomolecules modification [9-11]. Here we report the photochromic spiropyrans and spirooxazines containing these groups and their photochromic properties.

Results and Discussion.

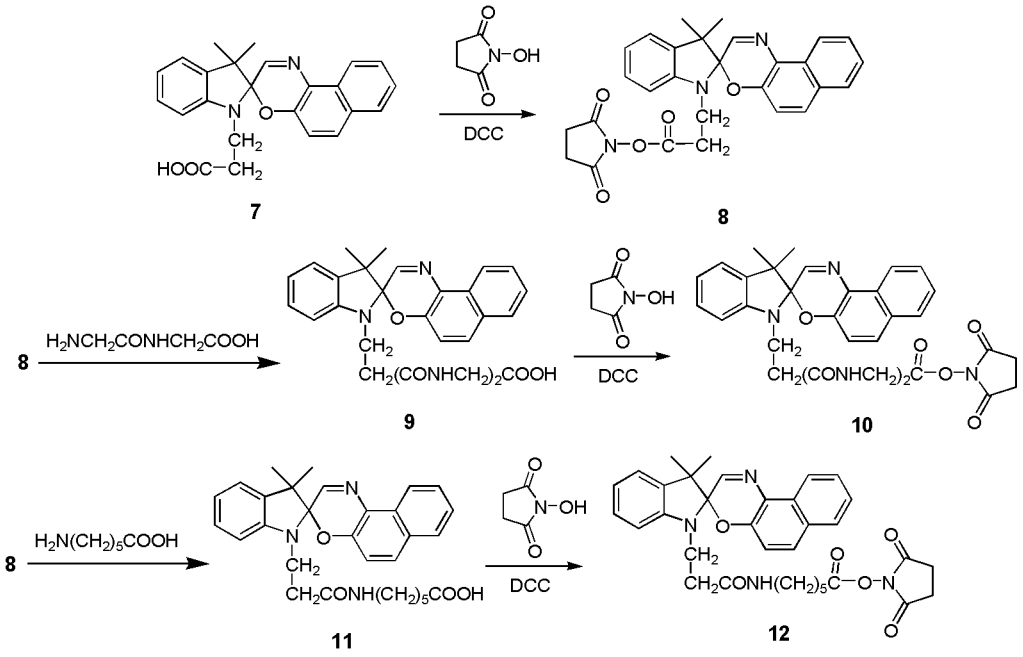
Synthesis.

The reference compounds **1** [12] and **7** [12] were synthesized according to the literatures and used as standards for comparisons with a series of spiropyrans and spirooxazines,

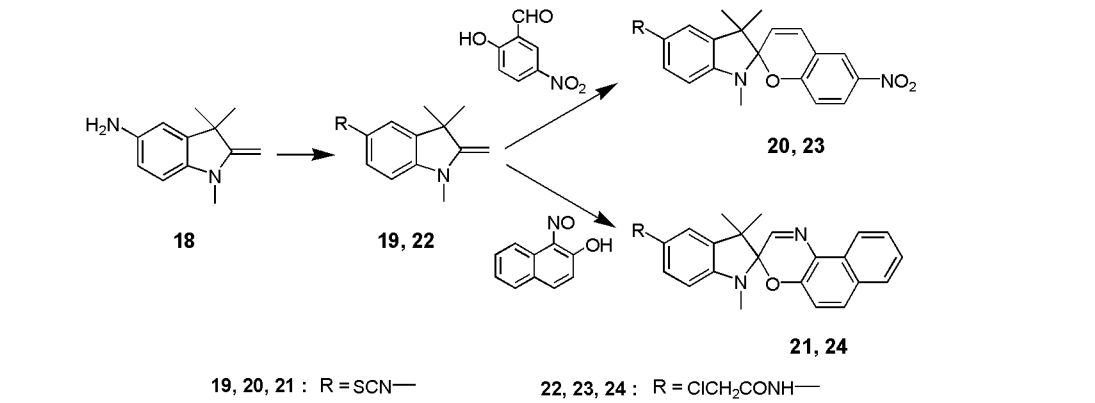
Scheme 2

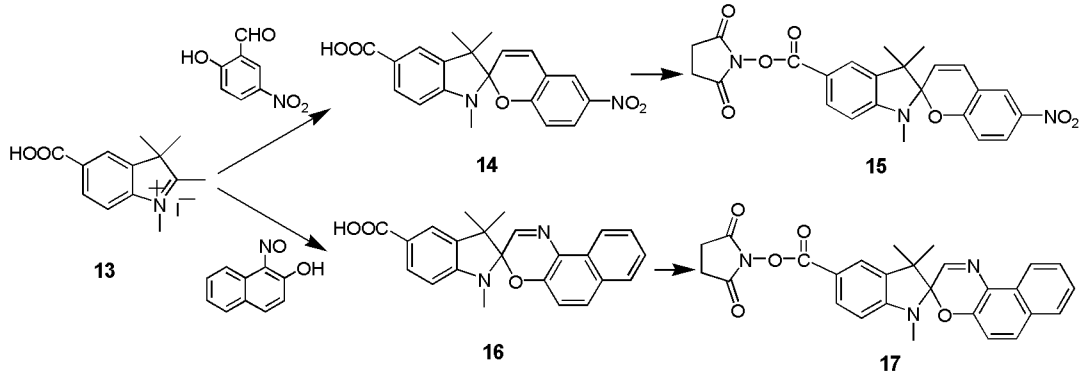


Scheme 2 (continued)



Scheme 3





respectively. Their structures and synthetic routes are shown in Schemes 2 and 3. The reactive pendant groups including carboxyl, succinimidyl ester, chloroacetyl and isothiocyanate, were connected to the indoline 1-nitrogen (**1**-**12**) or 5-carbon (**14**-**17**, **20**, **21**, **23** and **24**) of a photochromic spiro compound. The compounds **1** and **7**, which

have a carboxyl group, reacted with *N*-hydroxysuccinimide in the presence of DCC to form succinimidyl esters **2** and **8**, respectively. These esters reacted with various amino acids to give new compounds having a longer chain pendant group such as compounds **3**, **5**, **9** and **11** which were further converted in a similar manner into **4**, **6**, **10** and **12**, respectively. The functionalization at 5-carbon was carried out starting from 2-methylindoleninium iodide **13** and 2-methyleneindoline **18** (Scheme 3). The key intermediate isothiocyanate **19** and chloroacetylamide **22** were synthesized from the corresponding amine **18**. The structures of these functionalized spiro compounds were confirmed by their microanalytical and spectral data.

Photochromism.

The photochromic behaviors of the functionalized spiro compounds **1-12**, **14-17**, **20**, **21**, **23** and **24** were examined with the aid of electronic spectral measurements. They showed a broad band in the visible region (546-589 nm) by the irradiation of the ethanol solution with a high-pressure mercury lamp (Table 1), indicating the formation of their open colored form (PMC in Scheme 1). The absorption maxima of 1-substituted spiro compounds **2-6** and **8-12** appeared at similar wavelengths to those of the reference compounds **1** and **7**. The 5-substituted compounds **14, 15, 20**, **23** showed a shorter maxima than that of reference compounds **1** and the compounds **16, 17, 21**, **24** showed a shorter maxima than that of reference compounds **7**. As a typical example, the spectral chart of compound **4** in ethanol before and after irradiation for 30 seconds is shown in Figure 1.

Table 1

The Absorption Maxima (λ_{max}) of the Spiro-photochromic Compounds in Ethanol after Irradiation

Comp.	λ (nm)	Comp.	λ (nm)	Comp.	λ (nm)	Comp.	λ (nm)
1	575	**7**	587	**14**	560	**20**	562
2	578	**8**	589	**15**	564	**21**	571
3	569	**9**	576	**16**	572	**23**	546
4	576	**10**	577	**17**	575	**24**	570
5	570	**11**	575				
6	572	**12**	577				

A semiquantitative study of the decolorlization process of the open colored form of compound **2** was carried out. Figure 2 shows the decrease of the absorbance at the absorption maximum (578 nm) of the compound. The decolorization process of succinimidyl esters was found to be faster than the corresponding carboxyl compounds. Thus spirooxazine derivatives (**8-12**, **17**, **21** and **24**) decolorlized so fast that measurements were difficult on the available spectrophotometer.

In the solid state, the synthesized spiro compounds also showed a color change on irradiation. Figure 3 shows the solid UV-VIS reflection spectra of compound **4** before and

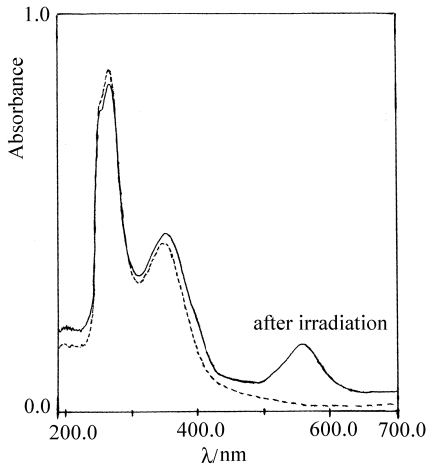


Figure 1. The absorption spectra of compound **4** in ethanol before and after irradiation.

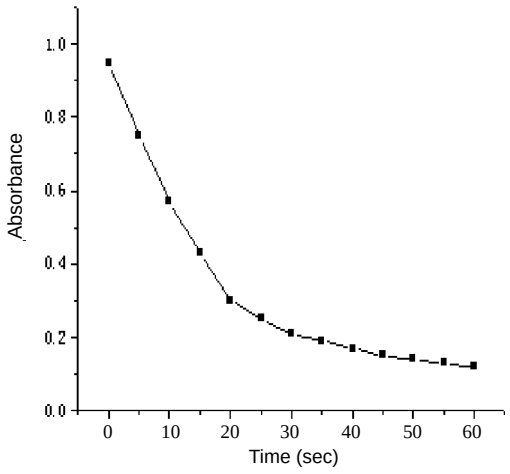


Figure 2. The intensity decrease at the absorption maximum (578 nm) of compound **2** after irradiation.

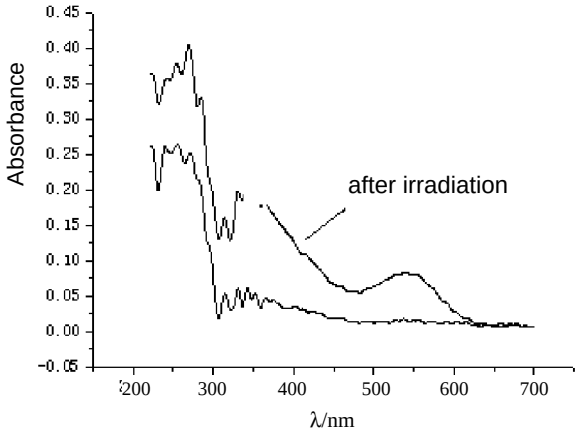


Figure 3. The solid UV-VIS reflection spectra of compound **4** before and after irradiation.

after irradiation. The maximum of this open colored form showed a blue shift compared to that in ethanol solution.

EXPERIMENTAL

General.

Melting points were determined with a Yanagimoto MP-35 melting point apparatus and are uncorrected. The ^{1}H nmr spectra were measured with a BRUKER AC-200 spectrometer using tetramethylsilane as the internal standard. Coupling constants are given in Hertz. The mass spectra were recorded on a 7070E-HE spectrometer operating in electron impact mode at 70 eV. The IR spectra were recorded on a Bio-Rad FTS135 spectrophotometer. A Yamaco CHN corder MT-3 apparatus was used for elemental analysis. A Shimadzu UV-240A and a 2101PC spectrometers were used for electronic absorption spectra and solid reflection spectra.

Synthesis of Spiro Compounds.

The starting materials were all commercially available. 5-Nitrosalicylaldehyde was prepared according to literature procedure [13]. Compounds **18** and **22** were synthesized as described previously [14].

N-Succinimidyl 3-[3,3-Dimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)]-1-yl]-propionate (**2**).

A mixture of 0.76 g (2 mmol) of compound **1**, 0.29 g (2.5 mmol) of *N*-hydroxysuccinimide and 0.52 g (2.5 mmol) of DCC (dicylohexylcarbodiimide) in 20 ml of dried dimethyl formamide (DMF) was stirred at room temperature for 24 hours. After evaporation of DMF *in vacuo*, the residue was dissolved in ethyl acetate, washed with a saturated sodium hydrocarbonate solution and then with water and purified by silica gel column chromatography (eluent, acetone:petroleum ether = 1:4, v:v) to give a yellow solid which was recrystallized from ethyl acetate-petroleum ether to give **2** as yellow crystals; 0.81 g (84%), mp 140-141°; ir (potassium bromide): ν 1732 (C=O),1605 (C=N),1275 (C-O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.22 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 2.89 (s, 4H, $2CH_2$), 3.00 (t, J=7.2Hz, 2H, CH_2), 3.73 (t, J=7.2Hz, 2H, CH_2), 6.00 (d, J=10.8Hz, 1H, vinyl-H), 6.68~7.38 (m, 6H, ArH and vinyl-H), 8.10 (m, 2H, ArH); ms: m/z 477 (M^+).

Anal. Cacld. for $C_{25}H_{23}N_3O_7$: C, 62.89; H, 4.86; N, 8.80. Found: C, 62.98; H, 4.74; N, 8.92.

3-[2-[3,3-Dimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)]-1-yl]]-propionylglycylglycine (**3**).

To a solution of 0.48 g (1 mmol) of compound **2** in 3 ml of DMF, 0.13 g (1 mmol) of glycylglycine in 4 ml of aqueous sodium hydrocarbonate solution was added and the mixture was stirred at room temperature for 6 hours. After evaporation *in vacuo*, 10 ml of 10% aqueous citric acid solution was added and the insoluble solid was collected by filtration, and recrystallized from acetone-petroleum ether to give **3** as a rose pink solid. 0.42 g (85%), mp 118-120°; ir (potassium bromide): ν 3400 (NH), 3050, 2920 (OH), 1720, 1660 (C=O), 1604 (C=N), 1270 (C-O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.16 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 2.62 (t, J=7.2Hz, 2H, CH_2), 3.40 (s, 2H, CH_2), 3.59 (t, J=7.2Hz, 2H, CH_2), 3.87 (s, 2H, CH_2), 6.10 (d, J=10.8Hz, 1H, vinyl-H), 6.72-7.39 (m, 6H, ArH and vinyl-H), 8.00-8.17 (m, 2H, ArH); ms: m/z 494 (M^+).

Anal. Cacld. for $C_{25}H_{26}N_4O_7$: C, 60.72; H, 5.30; N, 11.33. Found: C, 60.65; H, 5.23; N, 11.47.

N-Succinimidyl 3-[2-[3,3-Dimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)]-1-yl]]-propionylglycylglycinate (**4**).

The compound **4** was synthesized with the similar process to that for compound **2** from **3** and *N*-hydroxysuccinimide to give yellow crystals. 0.49 g (83%), mp 126-127°; ir (potassium bromide): ν 3380 (NH), 1735, 1700, 1660 (C=O), 1610 (C=N), 1270 (C-O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.18 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 2.52~2.65 (m, 2H, CH_2), 2.86 (s, 4H, $2CH_2$), 3.00~3.10 (m, 2H, CH_2), 3.60~3.72 (m, 2H, CH_2), 3.89 (s, 2H, CH_2), 6.00 (d, J=10,8Hz, 1H, vinyl-H), 6.74-7.28 (m, 6H, ArH and vinyl-H), 8.00-8.10 (m, 2H, ArH); ms: m/z 591 (M^+).

Anal. Cacld. for $C_{29}H_{29}N_5O_9$: C, 58.88; H, 4.94; N, 11.84. Found: C, 58.75; H, 4.93; N, 11.97.

6-[3-[3,3-Dimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)]-1-yl]propionylamino]-hexanoic Acid (**5**).

The compound **5** was synthesized with the similar process to that for compound **3** from **4** and 6-aminohexoic acid to give a rose pink solid. 0.42 g (85%), mp 80-81°; ir (potassium bromide): ν 3300 (NH), 3060, 2930 (OH), 1725, 1675 (C=O), 1615 (C=N), 1275(C-O) cm^{-1}; ^{1}H nmr (deuteriochloroform): ν 1.15 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.32-1.66 (m, 6H, $3CH_2$), 2.20-2.60 (m, 4H, $2CH_2$), 3.08-3.28 (m, 2H, CH_2), 3.50-3.68 (m, 2H, CH_2), 5.72 (br, 1H, NH), 5.89 (d, J=10.8Hz, 1H, vinyl-H), 6.65-7.25 (m, 6H, ArH and vinyl-H), 8.00-8.15 (m, 2H, ArH); ms: m/z 493 (M^+).

Anal. Cacld. for $C_{27}H_{31}N_3O_6$: C, 65.71; H, 6.33; N, 8.51. Found: C, 65.65 H, 6.38 N 8.57.

N-Succinimidyl 6-[3-[3,3-Dimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)]-1-yl]-propionylamino]-hexanoate (**6**).

The compound **6** was synthesized with the similar process to that for compound **2** from **5** and *N*-hydroxysuccinimide to give yellow crystals. 0.44 g (76%), mp 137-138°; ir (potassium bromide): ν 3300 (NH), 1782, 1735 (C=O), 1609 (C=N), 1275 (C-O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.15 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.34-1.48 (m, 4H, $2CH_2$), 1.60-1.82 (m, 2H, CH_2), 2.38-2.68 (m, 4H, $2CH_2$), 2.82 (s, 4H, $2CH_2$), 3.10~3.32 (m, 2H, CH_2), 3.50-3.70 (m, 2H, CH_2), 5.91 (d, J=10.8Hz, 1H, vinyl-H), 6.68-7.28 (m, 6H, ArH and vinyl-H), 8.04-8.12 (m, 2H, ArH); ms: m/z 590 (M^+).

Anal. Cacld. for $C_{31}H_{34}N_4O_8$: C, 63.04; H, 5.80; N, 9.49. Found: C, 63.12; H, 5.68; N, 9.40.

N-Succinimidyl 3-[3,3-Dimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine)]-1-yl]-propionate (**8**).

The compound **8** was synthesized with the similar process to that for compound **2** from **7** and *N*-hydroxysuccinimide to give white crystals. 0.78 g (82%), mp 184-185°; ir (potassium bromide): ν 1730 (C=O), 1615 (C=N), 1240 (C-O) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.30 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 2.80 (s, 4H, $2CH_2$), 3.00-3.12 (m, 2H, CH_2), 3.52-3.70 (m, 2H, CH_2), 6.68 (d, J=8.1Hz, 1H, vinyl-H), 6.94-7.81 (m, 9H, ArH), 8.57 (d, J=9.0Hz, 1H, ArH); ms: m/z 483 (M^+).

Anal. Cacld. for $C_{28}H_{25}N_3O_5$: C, 69.55; H, 5.21; N, 8.69. Found: C, 69.41; H, 5.26; N, 8.84.

3-[2-[3,3-Dimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine)]-1-yl]propionylglycylglycine (**9**).

The compound **9** was synthesized with the similar process to that for compound **3** from **8** and glycylglycine to give a rose pink solid. 0.45 g (90%), mp 110-112°; ir (potassium bromide): ν 3300

(NH), 3050, 2960 (OH), 1725, 1650 (C=O), 1601 (C=N), 1245 (C-O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.30 (s, 6H, $2CH_3$), 3.50-3.70 (m, 2H, CH_2), 3.82 (d, J= 5.6Hz, 4H, $2CH_2$), 4.00-4.20 (m, 2H, CH_2), 6.70-7.81 (m, 9H, ArH and vinyl-H), 8.08 (m, 1H, ArH), 8.54 (d, J=7.2Hz, 1H, ArH); ms: m/z 500 (M^+).

Anal. Cacld. for $C_{28}H_{28}N_4O_5$,: C, 67.19; H, 5.64; N, 11.19. Found: C, 67.25; H, 5.56; N, 11.27.

N-Succinimidyl 3-[2-[3,3-Dimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine)]-1-yl]propionyl-glycylglycinate (**10**).

The compound **10** was synthesized with the similar process to that for compound **2** from **9** and *N*-hydroxysuccinimide to give yellow crystals. 0.43 g (72%), mp 144-145°; ir (potassium bromide): ν 3320 (NH), 3060, 2970 (OH), 1765, 1735 (C=O), 1605 (C=N), 1240 (C-O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.31 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 2.82 (s, 4H, $2CH_2$), 3.34-3.58 (m, 2H, CH_2), 3.74-3.89 (m, 4H, $2CH_2$), 3.96-4.10 (m, 2H, CH_2), 6.67-7.98 (m, 10H, ArH and vinyl-H), 8.52 (d, J=7.2Hz, 1H); ms: m/z 597 (M^+).

Anal. Cacld. for $C_{32}H_{31}N_5O_7$: C, 64.31; H, 5.23; N, 11.72. Found: C, 64.25; H, 5.29; N, 11.67.

6-[3-[3,3-Dimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine)]-1-yl]propionylamino]-hexanoic Acid (**11**).

The compound **11** was synthesized with the similar process to that for compound **3** from **8** and 6-aminohexoic acid to give a rose pink solid. 0.42 g (84%), mp 86-88°; ir (potassium bromide): ν 3300 (NH), 3060, 2930 (OH), 1720, 1660 (C=O), 1604 (C=N), 1270 (C-O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.28 (s, 6H, $2CH_3$), 1.34-1.67 (m, 6H, $3CH_2$), 2.31-2.62 (m, 4H, $2CH_2$), 3.10-3.28 (m, 2H, CH_2), 3.52-3.66 (m, 2H, CH_2), 6.65-7.85 (m, 10H, ArH and vinyl-H), 8.54 (d, J=7.2Hz, 1H); ms: m/z 499 (M^+).

Anal. Cacld. for $C_{30}H_{33}N_3O_4$: C, 72.12; H, 6.66; N, 8.41. Found: C, 72.25; H, 6.53; N, 8.37.

N-Succinimidyl 6-[3-[3,3-Dimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine)]-1-yl]-propionylamino]-hexanoate (**12**).

The compound **12** was synthesized with the similar process to that for compound **2** from **11** and *N*-hydroxysuccinimide to give yellow crystals. 0.41 g (69%), mp 140-141°; ir (potassium bromide): ν 3350 (NH), 1780, 1725 (C=O), 1606 (C=N), 1240 (C-O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.24 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.36-1.65 (m, 6H, $3CH_2$), 2.28-2.60 (m, 4H, $2CH_2$), 2.87 (s, 4H, $2CH_2$), 3.15-3.32 (m, 2H, CH_2), 3.56-3.68 (m, 2H, CH_2), 6.70-7.81 (m, 10H, ArH, vinyl-H), 8.52 (d, J=7.2Hz, 1H); ms: m/z 596 (M^+).

Anal. Cacld. for $C_{34}H_{36}N_4O_6$: C, 68.44; H, 6.08; N, 9.39. Found: C, 68.59; H, 6.03; N, 9.47.

5-Carboxyl-1,2,3,3-tetramethylindoleninium Iodide (**13**).

To an aqueous concentrated hydrochloric acid (20 ml) and ice water (30 ml) of *p*-amino benzoic acid (6.8 g, 0.05 mol) was added an aqueous solution (18 ml) of sodium nitrite (3.5 g, 0.05 mol) at 0 °C. After 30 minutes of stirring, an aqueous concentrated hydrochloric acid solution (35 ml), and stannous chloride dihydrate (34 g, 0.15 mol) was added to the mixture at 0 °C. The reaction mixture was stirred for additional 30 minutes and filtered to give a milk white solid (*p*-carboxylphenylhydrazine hydrochloride). To a mixture of 3.6 g of this solid, 4.4 ml of 3-methyl-2-butanone in 40 ml ethanol, 2.4 ml of concentrated sulfuric acid was added. The mixture was refluxed for 7 hours. After evaporation of the solvent *in vacuo*, the residue was neutralized with an aqueous sodium carbonate solution and extracted with diethyl ether and the separated ether layer was dried with anhydrous magnesium sulfate. After evaporation of diethyl ether, the residue was added to 1.2 ml of iodomethane in 30 ml of chloroform. The mixture was refluxed for 5 hours under nitrogen atmosphere. The precipitate began to appear 1 hour later. After cooling, a white solid **13** (1.1 g) was collected by filtration and used for the next reaction without further purification.

1,3,3-Trimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)]-5-yl-formic Acid (**14**).

A mixture of 6.9 g of compound **13**, 3.3 g of 5-nitrosalicylaldehyde and 1.5 ml of piperidine in 50 ml ethanol was refluxed for 5 hours. After evaporation of solvent, the residue was purified by silica gel thin layer chromatography (eluent, acetone:petroleum ether = 1:2, v:v) to give a yellow solid which was recrystallized from acetone-petroleum ether to give **14** as yellow crystals. 3.1 g (42%), mp163-165°; ir (potassium bromide): ν 3300-2500 (OH), 1704 (C=O), 1614 (C=N), 1240 (C-O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.19 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 5.84 (d, J=5.4Hz, 1H, vinyl-H), 6.52-7.25 (m, 5H, ArH and vinyl-H), 7.75-8.00 (m, 2H, ArH)?ms: m/z 366 (M^+).

Anal. Cacld. for $C_{20}H_{18}N_2O_5$: C, 65.57; H, 4.95; N 7.65. Found: C, 65.62; H, 4.89; N, 7.72.

N-Succinimidyl 1,3,3-Trimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)]-5-yl-formate (**15**).

The compound **15** was synthesized with the similar process to that for compound **2** from **14** and *N*-hydroxysuccinimide to give yellow crystals. 0.78 g (85%), mp 128-129°; ir (potassium bromide): ν 1780 (C=O), 1620 (C=N), 1235 (C-O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.22 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 2.87 (s, 4H, $2CH_2$), 5.88, 5.91 (d, J=5.4Hz, 1H, vinyl-H), 6.60-7.15 (m, 5H, ArH and vinyl-H), 7.68~7.99 (m, 2H, ArH); ms: m/z 463 (M^+).

Anal. Cacld. for $C_{24}H_{21}N_3O_7$: C, 62.20; H, 4.57; N, 9.07. Found: C, 62.11; H, 4.64; N, 9.01.

1,3,3-Trimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine)]-5-yl-formic Acid (**16**).

To a solution of 2.8 g of 1-nitroso-2-naphthol in 20 ml of ethanol, a solution of 5.7 g of **13** and 4 ml trimethylamine in 20 ml ethanol was dropwise added. The mixture was refluxed for 5 hours. After evaporation of solvent, the residue was purified by silica gel thin layer chromatography (eluent, acetone:petroleum ether = 1:2, v:v) to give a yellow solid which was recrystallized from acetone-petroleum ether to give **16** as yellow crystals. 2.3g (38%), mp 158-160°; ir (potassium bromide): ν 3050, 2960 (OH), 1705 (C=O), 1615 (C=N), 1225 (C-O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.25 (s, 6H, $2CH_3$), 2.62 (s, 3H, CH_3), 6.63 (d, J=4.8Hz, 1H, vinyl-H), 6.90-7.80 (m, 8H, ArH), 8.62 (d, J=7.2Hz, 1H); ms: m/z 372 (M^+).

Anal. Cacld. for $C_{23}H_{20}N_2O_3$: C, 74.18; H, 5.41; N, 7.52. Found: C, 74.25; H, 5.36; N, 7.32.

N-Succinimidyl 1,3,3-Trimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine)]-5-yl-formate (**17**).

The compound **17** was synthesized with the similar process to that for compound **2** from **16** and *N*-hydroxysuccinimide to give

yellow crystals. 0.73 g (78%), mp 120-121°; ir (potassium bromide): ν 1765 (C=O), 1610 (C=N), 1220 (C-O) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.22 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 2.89 (s, 4H, $2CH_2$), 6.63 (d, J=4.8Hz, 1H, vinyl-H), 6.88-7.82 (m, 8H, ArH), 8.62 (d, J=7.2Hz, 1H, ArH); ms: m/z 469 (M^+).

Anal. Cacld. for $C_{27}H_{23}N_3O_5$: C, 69.07; H, 4.94; N, 8.95. Found: C, 69.25; H, 4.86; N, 8.87.

5-Isothiocyanato-1,3,3-trimethyl-2-methyleneindoline (**19**).

A mixture of 1.1 g of compound **18**, 0.84 ml of 25% aqueous ammonia and 0.42 ml of carbon disulfide was stirred. After a precipitate was formed, 0.3 ml of water was added and the mixture was stirred at 35-40 °C for 1 hour. The precipitate was collected by filtration and washed with 3% aqueous ammonium chloride solution and water, successively, to give a yellow solid. The solid was mixed with 5 ml of water and a sodium chloroacetic acid solution (0.56 g of chloroacetic acid dissolved in 0.6 ml of water and neutralized with a solution of 0.36 g of sodium carbonate in 1.4 ml of water). After stirrng for 10 minutes, 5 ml of water was added and the mixture was stirred at 35-40 °C for 1 hour. To the reaction mixture was added dropwise an aqueous zinc chloride solution (0.4 g of zinc chloride in 1.5 ml of water) keeping the pH 7-8 with 4 mol/l of aqueous sodium hydroxide solution. The reaction mixture was stirred for 3 hours. After cooling, the precipitate was filtered and extracted with dimethyl ether. Evaporation of the extract gave a yellow solid 0.8 g, which was used for the next reaction without further purification.

5-Isothiocyanato-3,3-dimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)] (**20**).

A mixture of 0.44 g of compound **19** and 0.34 g of 5-nitrosalicylaldehyde in 12 ml of ethanol was refluxed for 5 hours. After evaporation of the solvent, the residue was purified by silica gel thin layer chromatography (eluent, acetone:petroleum ether = 1:4, v:v) to give a yellow solid which was recrystallized from ethyl acetate-petroleum ether to give **20** as yellow crystals. 0.33 g (44%), mp 167-168°; ir (potassium bromide): ν 2120 (S=C=N), 1607 (C=N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.17 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 2.73 (s, 3H, CH_3), 5.83 (d, J=5.4Hz, 1H, vinyl-H), 6.43-7.25 (m, 5H, ArH and vinyl-H), 8.00-8.04 (m, 2H, ArH); ms: m/z 379 (M^+).

Anal. Cacld. for $C_{20}H_{17}N_3O_3S$: C, 63.31; H, 4.52; N, 11.07. Found: C, 63.25; H, 4.61; N, 11.02.

5-Isothiocyanate-1,3,3-trimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine (**21**).

A mixture of 0.44 g of compound **19** and 0.35 g of 1-nitroso-2-naphthol in 15 ml of ethanol was refluxed for 5 hours. After evaporation of the solvent, the residue was purified by silica gel thin layer chromatograph (eluent, acetone:petroleum ether = 1:2, v:v) to give a yellow solid which was recrystallized from ethyl acetate-petroleum ether to give **21** as yellow crystals. 0.27 g (36%), mp 142-143°; ir (potassium bromide): ν 2120 (S=C=N), 1615, 1605 (C=N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.22 (s, 6H, $2CH_3$), 2.72 (s, 3H, CH_3), 6.62 (d, J=4.8Hz, 1H, vinyl-H), 6.88-7.69 (m, 8H, ArH), 8.62 (d, J=7.2Hz, 1H, ArH); ms: m/z 385 (M^+).

Anal. Cacld. for $C_{23}H_{19}N_3OS$: C, 71.66; H, 4.97; N, 10.90. Found: C, 71.85; H, 4.86; N, 10.82.

5-Chloroacetylamino-3,3-dimethyl-6'-nitrospiro[2'*H*-chromene-2,2'-(2,3-dihydro-1*H*-indole)] (**23**).

The compound **23** was synthesized with the similar process to that for compound **20** from **22** and 5-nitrosalicylaldehyde to give orange crystals. 0.38 g (47%), mp196-198°; ir (potassium bromide): ν 1659 (C=O), 1605 (C=N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.26 (s, 6H, $2CH_3$), 2.65 (s, 3H, CH_3), 4.20 (s, 2H, CH_2) 5.83 (d, J=5.4Hz, 1H, vinyl-H), 6.50~7.35 (m, 5H, ArH and vinyl-H), 8.00-8.04 (m, 2H, ArH); ms: m/z 413 (M^+).

Anal. Cacld. for $C_{21}H_{20}ClN_3O_4$: C, 60.95; H, 4.87; N, 10.15. Found: C, 61.06; H, 4.79; N, 10.08.

5-Chloroacetylamino-1,3,3-trimethylspiro[2,3-dihydro-1*H*-indole-2,3'-(3'*H*-naphtho[2,1-*b*][1,4]oxazine] (**24**).

The compound **24** was synthesized with the similar process to that for compound **21** from **22** and 1-nitroso-2-naphthol to give yellow crystals. 0.31 g (37%) mp184-185°; ir (potassium bromide): ν 1670 (C=O), 1605 (C=N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.24 (s, 6H, $2CH_3$), 2.70 (s, 3H, CH_3), 4.25 (s, 2H, CH_2), 6.60 (d, J=4.8Hz, 1H, vinyl-H), 6.90~7.71 (m, 8H, ArH), 8.64 (d, J=7.2Hz, 1H, ArH); ms: m/z 419 (M^+).

Anal. Cacld. for $C_{24}H_{22}ClN_3O_2$, C 68.65 H 5.28 N 10.01, Found: C 68.75 H 5.16 N 10.12.

The Spectroscopic Properties Determination of Photochromic Compounds.

The absorption spectra of photochromic compounds **1-12**, **14-17**, **20**, **21**, **23** and **24** in ethanol solution with the concentration of 10^{-5} mol/l after irradiation with a 400W high-pressure lamp for 30 seconds were recorded on a UV-240A spectrophotometer. The maxima of the open colored form of the compounds were listed in Table1.

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