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Synthesis and photochromic properties of phenanthropyran derivative substituted with styryl group

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Abstract

The synthesis and the photochromic properties of new phenanthropyran derivative containing styryl substituent are described. The compound **8** showed two-step two-photon photochromism to produce a thermally stable cyclopentaannulated compound **10** through a thermally unstable open keto form intermediate **9**.

Keywords: Photochromism; Phenanthropyran; Styryl substituent; Cyclopentaannulated compound

1. Introduction

Photochromism is defined as a reversible transformation of a compound between two isomers that have different optical properties upon photoirradiation. Photochromic molecules have been the subject of intense research because of their potential applications, which include ophthalmic lenses, optical storage media, photoswitching devices, etc. [1]. Many organic photochromic molecular systems have been explored such as diarylethenes [2], fulgides [3], spiropyrans [4], and spiroxazines [4,5]. Among them, 2H-1-benzopyran(2H-chromene) derivatives are most widely studied owing to their important color and dipole-moment changes [6]. These molecules change color from colorless to yellow or orange upon UV irradiation. The photochromic behavior is based on a photoinduced reversible opening of the pyran ring that converts the colorless form (the 'closed form') in a set of photoisomers where the pyran ring is opened (the 'open form') (Scheme 1).

The open colored forms are usually short-lived states because of the poor thermal stability. The main strategies to improve the photochromic properties of the 2H-1-benzopyrans involve the modification of the structures through fusion of five- or six-membered heteroaromatic rings to the 5,6- or 7,8-positions and the appropriate substitution on the molecule; namely, the introduction of bulky or aromatic substituents at the 2-position of the pyran ring [7].

We report herein the synthesis and the photochromic properties of novel phenanthropyran derivative with conjugative styryl substituent at 2-position to increase the stability of open form [8].

2. Experimental

2.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300 and Bruker AM-500 spectrometers with chemical shifts being referenced against TMS as an internal standard or the signal of the solvent $CDCl_3$. UV–vis absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer. Photoreaction was carried out using RPR-100 photochemical reactor (Southern New England Ultraviolet Co.) and Vilber

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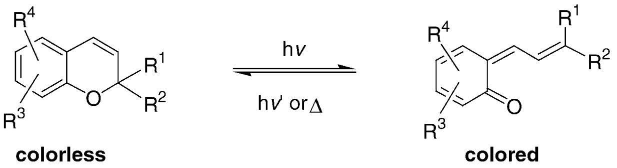


Scheme 1.

Lourmat UV-Lamp (4 W; intensity, 7 mW/cm^2). Mass spectra were determined with a Autospec MS spectrometer (Micromass Co.) by the electron impact (EI) method. FT-IR spectra were recorded on a Digilab FTS-165 spectrometer in KBr pellets and NaCl cell. Thin layer chromatography (TLC) was performed on Merk glass-backed silica gel 60 F_{254} plates. Purification of the reaction products was carried out by flash column chromatography using a glass column, dry packed with silica gel (230–400 mesh). Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents were used for UV absorption spectra.

2.2. Synthesis of 9-phenanthrol acetate **2**

Triethylamine (4.6 ml, 33.4 mmol) was added to a solution of 9-phenanthrol (5.0 g, 25.7 mmol) in CH_2Cl_2 (50 ml) at 0 °C under nitrogen atmosphere. A solution of acetyl chloride (2.0 ml, 28.4 mmol) in CH_2Cl_2 (10 ml) was added dropwise to the resulting solution and the mixture was stirred at 0 °C for 30 min. Water (50 ml) was added to the solution and extracted with CH_2Cl_2 (2 × 100 ml). The combined CH_2Cl_2 solution was washed with water (60 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (5:1 (v/v)) as an eluent gave **2** (5.77 g, 95% yield) as a white solid; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 2.50 (3H, s), 7.53 (1H, s), 7.58–7.70 (4H, m), 7.83 (1H, d, *J* = 8.4 Hz), 7.95 (1H, d, *J* = 8.6 Hz), 8.63 (1H, d, *J* = 10.2 Hz), 8.72 (1H, d, *J* = 9.4 Hz).

2.3. Synthesis of 10-acetyl-9-phenanthrol **3**

$AlCl_3$ (9.3 g, 69.9 mmol) was slowly added to a solution of 9-phenanthrol acetate **2** (5.5 g, 23.3 mmol) in nitrobenzene (15 ml) at room temperature. The resulting solution was stirred at room temperature for 15 h. Water (100 ml) was added to the solution, and extracted with ethyl acetate (2 × 150 ml). The combined ethyl acetate layer was washed with water (70 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (10:1 (v/v)) as an eluent gave **3** (3.73 g, 68% yield) as a white solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 2.80 (3H, s), 7.47 (1H, dd), 7.53 (1H, dd), 7.61 (1H, dd), 7.75 (1H, dd), 7.95 (1H, d, *J* = 8.2 Hz), 8.49 (1H, d, *J* = 7.4 Hz), 8.51 (1H, d, *J* = 8.1 Hz), 8.53 (1H, d, *J* = 9.4 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 31.69, 112.01, 122.39, 123.28, 124.46, 125.34, 125.39, 125.42, 126.09, 127.05, 127.15, 129.67, 130.95, 134.05, 162.90, 203.91; MS (*m/z*, %) = 236 (90), 221 (100), 189 (18), 165 (80), 139 (13), 82 (36); HRMS (M^+) calculated for $C_{16}H_{12}O_2$ 236.0837, found 236.0829.

2.4. Synthesis of 2-dimethoxymethyl-2-methyl-2,3-dihydro-2H-phenanthro [9,10-b]pyran-4-one **4**

Pyruvic aldehyde dimethyl acetal (2.0 ml, 16.5 mmol) and pyrrolidine (0.32 ml, 3.8 mmol) were added to a solution of 10-acetyl-9-phenanthrol **3** (3.0 g, 12.7 mmol) in toluene (30 ml) at room temperature. The resulting solution was refluxed for 4 h using Dean–Stark trap. The reaction mixture was cooled to room temperature and ethyl acetate (100 ml) was added to the solution. The resulting solution was washed with water (50 ml), brine (30 ml) and dried (Na_2SO_4), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (10:1 (v/v)) as an eluent gave **4** (2.98 g, 70% yield) as a white solid; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 1.53 (3H, s), 2.77 (1H, d, *J* = 16.0 Hz), 3.19 (1H, d, *J* = 16.0 Hz), 3.56 (6H, s), 4.48 (1H, s), 7.52 (1H, m), 7.61 (2H, m), 7.74 (1H, m), 8.38 (1H, dd, *J* = 8.0, 1.2 Hz), 8.52 (1H, d, *J* = 8.1 Hz), 8.57 (1H, d, *J* = 8.2 Hz), 9.52 (1H, dd, *J* = 8.4, 0.9 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 18.89, 43.94, 57.96 (2C), 83.57, 108.07, 109.13, 122.19, 122.66, 124.38, 125.03, 125.12, 126.10, 126.34, 126.85, 128.45, 129.05, 130.36, 134.35, 158.50, 193.04; MS (*m/z*, %) = 336 (34), 261 (22), 245 (22), 221 (37), 202 (33); HRMS (M^+) calculated for $C_{21}H_{20}O_4$ 336.1361, found 336.1366.

2.5. Synthesis of 2-dimethoxymethyl-2-methyl-4-hydroxy-3,4-dihydro-2H-phenanthro[9,10-b]pyran **5**

$NaBH_4$ (0.31 g, 8.3 mmol) was slowly added to a solution of 2-dimethoxymethyl-2-methyl-2,3-dihydro-2H-phenanthro[9,10-b]pyran-4-one **4** (2.8 g, 8.3 mmol) in methanol (20 ml) at 0 °C. The resulting solution was stirred at 0 °C for 0.5 h. Water (100 ml) was added to the solution, and extracted with ethyl acetate (2 × 100 ml). The combined ethyl acetate was washed with water (50 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (3:1 (v/v)) as an eluent gave diastereomeric mixture **5** (2.62 g, 70% yield) as a colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 1.55 (3H, s), 2.11 (2H, m), 2.30 (1H, dd, *J* = 14.6, 2.6 Hz), 2.38 (1H, dd, *J* = 14.6, 5.0 Hz), 2.67 (1H, dd, *J* = 15.2, 2.0 Hz), 3.23 (3H, s), 3.44 (3H, s), 3.61 (3H, s), 3.64 (3H, s), 3.93 (1H, d, *J* = 9.0 Hz), 4.34 (1H, s), 4.45 (1H, s), 5.19 (1H, m), 5.39 (1H, m), 7.49 (2H, dd, *J* = 7.7, 7.2 Hz), 7.58–7.67 (6H, m), 8.15 (1H, d, *J* = 8.2 Hz), 8.22 (1H, d, *J* = 8.2 Hz), 8.34 (1H, dd, *J* = 8.2, 1.2 Hz), 8.37 (1H, dd, *J* = 8.2, 1.2 Hz), 8.58–8.63 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 19.56, 24.94, 34.62, 36.10, 57.60, 57.95, 59.55, 60.65, 77.16, 78.74, 109.31, 110.10, 110.58, 111.23, 122.37, 122.40, 122.55, 122.64, 122.86, 122.98, 123.09, 123.66, 124.00, 124.13, 125.63, 126.10, 126.37, 126.48 (2C), 126.51, 127.18, 127.25, 127.34 (2C), 127.44 (2C), 131.31, 131.38, 131.45, 131.66, 146.10, 146.35; MS (*m/z*, %) = 338 (100), 321 (9), 274 (13), 263 (26), 245 (32), 221 (65), 165 (33); HRMS (M^+) calculated for $C_{21}H_{22}O_4$ 338.1518, found 338.1512.

*2.6. Synthesis of 2-dimethoxymethyl-2-methyl-2H-phenanthro[9,10-b]pyran **6***

To a solution of 2-dimethoxymethyl-2-methyl-4-hydroxy-3,4-dihydro-2H-phenanthro[9,10-b]pyran **5** (2.5 g, 7.4 mmol) in CH_2Cl_2 (30 ml) were added *N*,*N*-diisopropylethylamine (3.2 ml, 18.5 mmol) and methanesulfonyl chloride (0.66 ml, 8.50 mmol) at room temperature. The resulting solution was stirred for 16 h at room temperature and refluxed for 2 h. The reaction mixture was cooled to room temperature and CH_2Cl_2 (100 ml) was added to the solution. The resulting solution was washed with water (70 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (10:1 (v/v)) as an eluent gave **6** (2.06 g, 87% yield) as an orange color oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 1.53 (3H, s), 3.48 (3H, s), 3.52 (3H, s), 4.44 (1H, s), 5.87 (1H, d, J = 10.0 Hz), 7.16 (1H, d, J = 10.0 Hz), 7.52 (1H, dd, J = 8.1, 7.0 Hz), 7.57–7.63 (3H, m), 8.02 (1H, d, J = 8.1 Hz), 8.35 (1H, d, J = 7.7 Hz), 8.61 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 20.30, 57.66, 58.51, 80.31, 107.98, 110.16, 119.67, 121.80, 122.36, 122.51, 122.95, 124.17, 125.01, 125.31, 126.33, 126.53, 126.98, 127.04, 129.08, 131.07, 145.99; MS (*m/z*, %) = 320 (22), 306 (8), 289 (15), 259 (21), 245 (50), 202 (15); HRMS (M^+) calculated for $C_{21}H_{20}O_3$ 320.1412, found 320.1421.

*2.7. Synthesis of 2-methyl-2H-phenanthro[9,10-b]-pyran-2-carbaldehyde **7***

Sodium iodide (0.56 g, 3.75 mmol) and chlorotrimethylsilane (0.47 ml, 3.75 mmol) were added to a solution of 2-dimethoxymethyl-2-methyl-2H-phenanthro[9,10-b]pyran **6** (1.0 g, 3.12 mmol) in dioxane–acetonitrile (3:1) (30 ml) at room temperature. The resulting solution was stirred for 3 h at room temperature. Water (70 ml) was added to the solution, and extracted with ethyl acetate (2 × 60 ml). The combined ethyl acetate layer was washed with water (50 ml) and brine (30 ml), dried (Na_2SO_4), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (5:1 (v/v)) as an eluent gave **7** (0.47 g, 55% yield) as a brownish oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 1.61 (3H, s), 5.76 (1H, d, J = 9.8 Hz), 7.24 (1H, d, J = 9.8 Hz), 7.49–7.68 (4H, m), 7.99 (1H, d, J = 7.8 Hz), 8.41 (1H, d, J = 7.9 Hz), 8.60 (2H, d, J = 7.8 Hz), 9.89 (1H, s).

*2.8. Synthesis of 2-methyl-2-styryl-2H-phenanthro[9,10-b]pyran **8***

n-BuLi (1.6 M solution in hexane)(0.74 ml, 1.2 mmol) was slowly added to a solution of benzyltriphenylphosphonium bromide (0.59 g, 1.37 mmol) in tetrahydrofuran (10 ml) at 0 °C. 2-Methyl-2H-phenanthro[9,10-b]pyran-2-carbaldehyde **7** (0.25 g, 0.91 mmol) in tetrahydrofuran (3 ml) was added dropwise to the resulting solution and the mixture was stirred at 0 °C for 3 h. Water (30 ml) was added to the solution and was extracted with ethyl acetate (3 × 30 ml). The combined ethyl acetate solution was washed with water (20 ml) and brine (20 ml), dried ($MgSO_4$), and concentrated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (10:1 (v/v)) as an eluent gave **8** (0.21 g, 67% yield, Z/E = 3.9); E-isomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 1.78 (3H, s), 5.86 (1H, d, J = 9.8 Hz), 6.37 (1H, d, J = 16.1 Hz), 6.65 (1H, d, J = 16.1 Hz), 7.15–7.29 (6H, m), 7.50–7.65 (4H, m), 8.02 (1H, d, J = 8.4 Hz), 8.43 (1H, d, J = 9.6 Hz), 8.61 (2H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 27.23, 77.88, 110.34, 118.57, 119.83, 121.80, 122.51, 122.57, 123.06, 124.14, 125.66, 126.13, 126.42, 126.56, 126.60, 126.94, 127.07, 127.65, 128.42, 129.20, 129.29, 131.16, 131.65, 135.79, 136.46, 146.61; MS (*m/z*, %) = 348 (100), 333 (61), 277 (17), 263 (18), 245 (40), 202 (11), 183 (13); HRMS (M^+) calculated for $C_{26}H_{20}O$ 348.1514, found 348.1531; Z-isomer: ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 1.65 (3H, s), 5.68 (1H, d, J = 9.8 Hz), 5.97 (1H, d, J = 12.6 Hz), 6.62 (1H, d, J = 12.6 Hz), 6.89 (1H, d, J = 9.8 Hz), 7.17–7.30 (5H, m), 7.52–7.66 (4H, m), 7.93 (1H, d, J = 8.3 Hz), 8.45 (1H, d, J = 7.1 Hz), 8.63 (2H, d, J = 8.3 Hz): MS (*m/z*, %) = 348 (100), 333 (55), 307 (10), 289 (10), 277 (25), 146 (35); HRMS (M^+) calculated for $C_{26}H_{20}O$ 348.1514, found 348.1532.

*2.9. Irradiation of 2-methyl-2-styryl-2H-phenanthro[9,10-b]pyran **8***

Deaerated solution of 2-methyl-2-styryl-2H-phenanthro[9,10-b]pyran **8** (40 mg, 0.115 mmol) in methanol (5 ml) was irradiated in a Rayonet photochemical reactor, model RPR-100, equipped with 436 nm lamps and UV-lamp (4 W; intensity, 7 mW/cm^2) with 254 nm lamp simultaneously. After irradiation for 5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoproduct **10** was isolated in 22 mg (55% yield) by column chromatography with *n*-hexane/ethyl acetate (15:1, v/v) as an eluent as a white solid. **10**; ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 2.08 (3H, s), 4.15 (1H, m), 4.43 (1H, dd, J = 8.4, 2.1 Hz), 5.58 (1H, s), 6.11 (1H, d, J = 8.4 Hz), 7.33 (3H, m), 7.44 (2H, m), 7.50 (1H, m), 7.56–7.67 (4H, m), 8.14 (1H, dd, J = 7.5, 1.8 Hz), 8.67 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 14.08, 55.14, 58.58, 95.39, 117.33, 122.44, 122.61, 123.00, 123.35, 123.47, 123.65, 126.46, 126.68,

Table 1
Crystal data and structure refinement for the compound **10**

Empirical formula	$C_{26}H_{20}O$
Formula weight	348.42
Temperature (K)	295 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$p\bar{1}$
Unit cell dimensions	a = 9.210 (3) Å, α = 70.44 (4)°; b = 10.305 (8) Å, β = 66.39 (3)°; c = 11.390 (5)° Å, γ = 79.94 (5)
Volume (Å^3), Z	932.3 (9), 2
Density (calculated) (Mg/m^3)	1.241
Absorption coefficient (mm^{-1})	0.074
F(0 0 0)	368
Crystal size	0.41 mm × 0.32 mm × 0.38 mm
Theta range for data collection (°)	2.10–26.00
Limiting indices	$-1\leq h \leq 11$, $-12\leq k \leq 12$, $-13\leq l \leq 14$
Reflections collected	4271
Independent reflections	3581 [R(int) = 0.0373]
Completeness to θ = 26.00° (%)	97.8
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3581/0/244
Goodness-of-fit on F^2	1.206
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0973, wR_2 = 0.1947
R indices (all data)	R_1 = 0.1259, wR_2 = 0.2194
Largest diff. peak and hole (Å^{-3})	0.769 and −0.623e

126.77, 127.07, 127.23, 127.59, 127.6, 128.8, 128.9, 129.9, 131.5, 133.2, 138.7, 144.8, 151.3; UV (methanol) λ_{max} 309, 257, 222 nm; FT-IR (KBr) 3026.0, 2932.6, 1607.6, 1449.9, 1361.3, 1090.0, 1029.5, 939.0, 750.0, 723.5, 698.5 cm^{-1}; MS (m/z, %) = 348 (100), 333 (55), 307 (10), 289 (10), 245 (25); HRMS (M$^+$) calculated for $C_{26}H_{20}O$ 348.1514, found 348.1515.

2.10. *Irradiation of the compound **10***

Deaerated solution of the compound **10** (20 mg, 0.057 mmol) in methanol (5 ml) was irradiated in a Rayonet photochemical reactor, model RPR-100, equipped with 300 nm lamps. After irradiation for 20 min, the resulting photoreaction mixture was concentrated in vacuo. 2-Methyl-2-styryl-2H-phenanthro[9,10-b]pyran **8** was isolated in 36% yield (7.2 mg) by column chromatography with *n*-hexane/ethyl acetate (10:1 (v/v)) as an eluent.

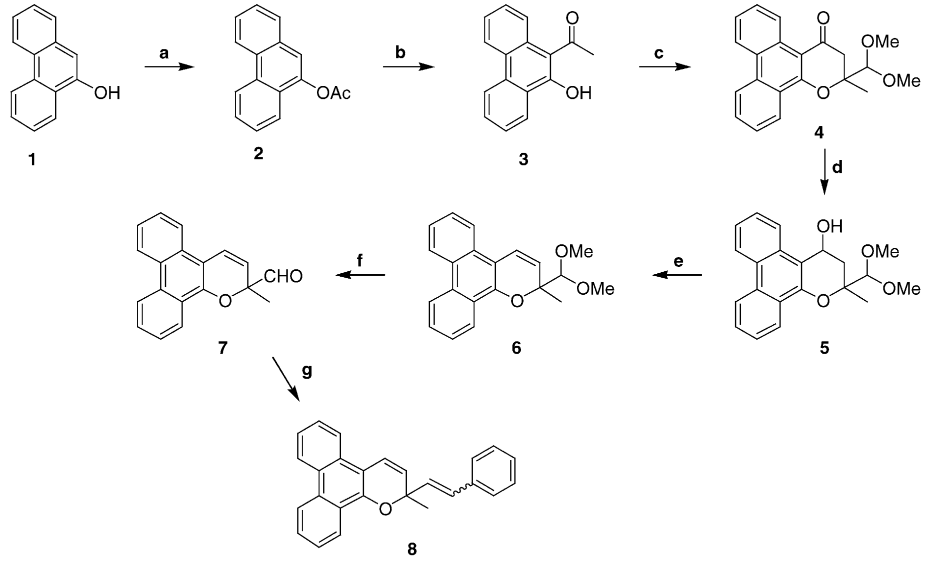
2.11. *Crystal structure determination of the compound **10***

Single crystals of the compound **10** suitable for X-ray diffraction were obtained by cooling of its methanol solution.

3. Results and discussion

3.1. *Synthesis of 2-methyl-2-styryl-2H-phenanthro[9,10-b] pyran **8***

The synthetic pathway for the preparation of the phenanthropyran derivative **8** is described in Scheme 2. First, the pyrrolidine-catalyzed Kabbe condensation [9] of compound **3**, prepared from 9-phenanthrol **1** via Fries rearrangement, with pyruvic aldehyde dimethylacetal gave cyclized compound **4** in good yield. Sodium borohydride reduction of keto compound **4** in methanol at 0 °C produced alcohol compound **5**. The 2H-phenanthro[9,10-*b*]pyran compound **6** was obtained by the conversion of the alcohol compound **5** to



Scheme 2. Reagents and conditions: (a) AcCl, Et_3N, CH_2Cl_2, 0 °C, 30 min, 95%; (b) $AlCl_3$, nitrobenzene, rt, 15 h, 68%; (c) Pyruvic aldehyde dimethylacetal, pyrrolidine, toluene, reflux, 4 h, 70%; (d) $NaBH_4$, MeOH, 0 °C, 30 min, 70%; (e) MsCl, $(i\text{-}Pr)_2NEt$, CH_2Cl_2, rt → reflux, 2 h, 87%; (f) NaI, TMSCl, dioxane–CH_3CN (3:1), rt, 3 h, 55%; (g) benzyl triphenylphosphonium bromide, *n*-BuLi, THF, 0 °C, 67%.

mesylated derivatives using methanesulfonyl chloride and Hünig base in CH_2Cl_2 followed by refluxing for 2 h in situ. Hydrolysis of acetal group of the compound **6** with NaI/TMSCl [10] afforded corresponding aldehyde compound **7**. Finally, C-2 styryl group substituted phenanthropyran compound **8** was prepared as a E/Z isomeric mixture by Wittig reaction with benzyltriphenylphosphonium bromide.

3.2. Photochromic properties of 2-methyl-2-styryl-2H-phenanthro[9,10-b]pyran ***8***

The photochromic behavior of synthetic phenanthropyran derivative **8** was studied. Fig. 1 represents the absorption spectral change of the compound **8** in methanol by photoirradiation. The original solution was colorless and had an absorption maxima at 256 and 342 nm. When the methanol solution of the colorless ring closed form was irradiated with 254 nm UV light, new absorption maximum at 447 nm appeared and the solution turned orange. It is thought that the photo-generated 447 nm band is due to the ring-open form **9** (Scheme 3). The ring-opening reaction was too fast to measure the absorption spectral change. The absorption of the ring-closed form appears at a shorter wavelength, while the absorption of the ring-open form takes place at a longer wavelength due to an extension of the π-conjugation. The open form compound **9** could be reversed back to closed form, and consequently the orange color was bleached, by irradiation with visible light or by thermal reaction in the dark. The orange color persisted over 2 days in the dark, although it took as much as 30 min to convert back to the original state in the visible light. The compound **8** was initially a Z/E isomeric mixture in a ratio of 3.9:1, but the photoirradiation and bleaching produced more stable E isomer only.

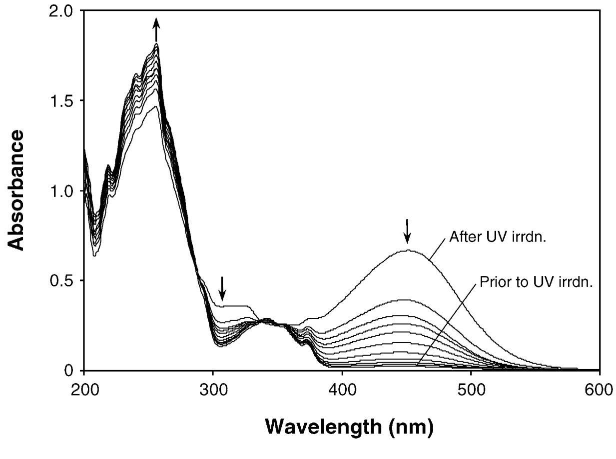


Fig. 1. Absorption spectral changes of **8** in methanol (2.5 × 10^{-5} mol/l) before and after UV irradiation with UV lamp (4 W; intensity, 7 mW/cm^2) at 254 nm. Photochromic bleaching is monitored over 30 min at intervals of 3 min.

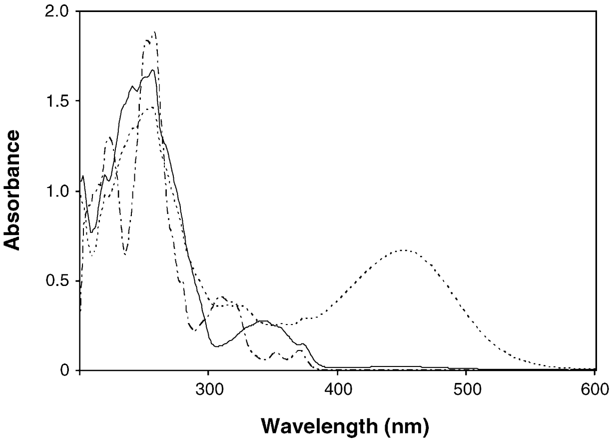
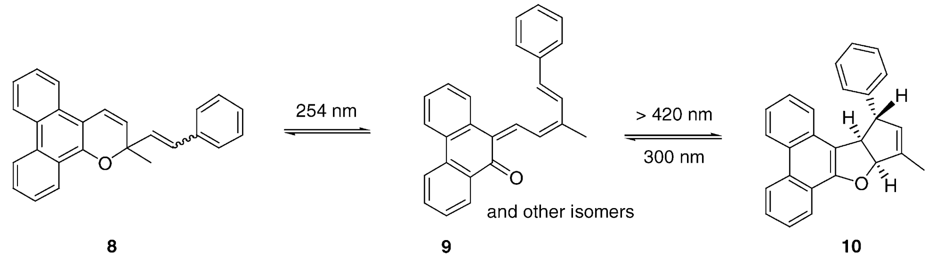


Fig. 2. Absorption spectra in methanol (2.5 × 10^{-5} mol/l): (—) original sample **8**; (- - -) **9**, after UV irradiation with 254 nm; (- · -) **10**, after irradiation with 254 and 436 nm light.

We further found that the above phenanthropyran derivative **8** substituted with styryl group at 2-position showed an interesting photochromic reaction upon irradiation simultaneously at two wavelengths (254 and 436 nm) in methanol. Upon irradiation of the colorless solution of the compound **8** with UV light (254 and 436 nm) for 5 h, absorption maximum at 447 nm due to the open keto form **9** decreased, whereas new three absorption maxima at 222, 257, and 309 nm could be seen as shown in Fig. 2. The new photogenerated product was thermally stable and could be isolated by column chromatography.

The structure of the compound **10** (Table 1) was determined by various spectroscopic methods including ^1H–^1H and ^1H–^{13}C correlation spectroscopy (COSY), HMBC, nuclear Overhauser and exchange spectroscopy (NOESY) (Table 2) and finally X-ray crystallographic analysis. The ^1H–^1H and ^1H–^{13}C correlation spectroscopy (COSY) spectra of **10** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **10**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Table 2. In order to determine the location of the quaternary carbon, the HMBC spectrum of **10** was taken. The presence of the cross-peaks due to the vicinal coupling between the protons of C(1) and C(2) and the quaternary carbon C(4) in 10 showed the cyclopentaannulated structure for the compound **10**. In the same manner, the presence of the cross-peaks due to the vicinal coupling between the protons of C(1) and C(5) and the carbon C(3) in **10** also showed the cyclopentaannulated structure. The 3D-structure of **10** was determined by a nuclear overhauser and exchange spectroscopy (NOESY). In particular, the presence of the cross-peak between the proton of C(1) and the proton of C(5) in **10** showed the close proximity of the proton of C(1) to the proton of C(5) indicating that these protons are located on the same side of the molecule. Thus, the skeletal structure of **10** was unambiguously established as shown in Fig. 3.

The novel cyclopentaannulated structure was again confirmed by X-ray crystallographic analysis as shown in Table 1 and Fig. 4. The cyclopentaannulated compound **10** returned to the initial phenanthropyran form by irradiation with 300 nm



Scheme 3. .

Table 2
Some characteristic ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz), COSY, NOESY, and HMBC data for the compound **10** in $CDCl_3$[a]

Position	δ_C (ppm)	M[b]	δ_H (ppm)	I[c]	M[d]	J_{H-H} (Hz)	COSY	NOESY	HMBC[e]
1	58.6	d	4.43	1H	dd	8.4 (J_{1H-5H}), 2.1 (J_{1H-2H})	H2, H5	H2, H5	H3, H5
2	55.1	d	4.15	1H	m		H1, H3, H5	H1, H3	H1, H3, H5
3	133.2	d	5.58	1H	d	0.7 (J_{3H-2H})	H2	H2, H6	H1, H2, H5
4	138.7	s							H1, H2, H3, H5
5	95.4	d	6.11	1H	dd	8.4 (J_{5H-1H}), 1.2 (J_{5H-2H})	H1, H2	H1, H6	H1, H2, H3, H6
6	14.1	q	2.08	3H	s			H3, H5	H3, H5

[a] All these assignments were confirmed by ^{1}H–^{1}H and ^{1}H–^{13}C COSY and NOESY, HMBC spectra.
[b] Multiplicities were determined by DEPT spectrum.
[c] Integrated intensity.
[d] Multiplicities.
[e] Protons correlated to carbon resonances in ^{13}C column.

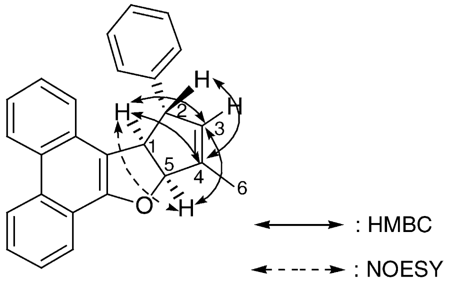


Fig. 3. Important correlations observed in HMBC and NOESY spectra of the compound **10**.

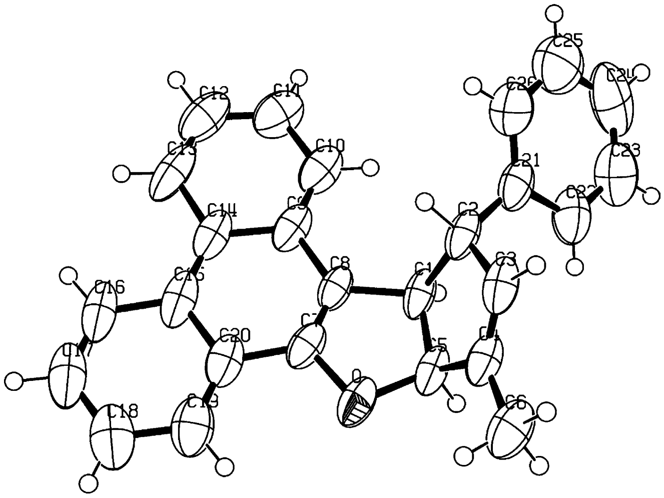


Fig. 4. X-ray structure of compound **10**.

light. Irradiation of deaerated solution of the cyclopentaannulated compound **10** in methanol using Rayonet photochemical reactor with 300 nm lamps for 20 min gave 2-methyl-2-styryl-2H-phenanthro[9,10-b]pyran **8** in 36% yield. This styryl group substituted phenanthropyran derivative is thus regarded as a two-photon photochromic system, in which photochromic reactions proceed between isomers via an unstable intermediate in a two-step, two-photon process [11].

In summary, new photochromic compound of the phenanthopyran derivative containing styryl substituent has been synthesized from 9-phenanthrol. The styryl group was introduced by Wittig olefination reaction. They showed photochromic behavior, changed from colorless to orange upon irradiation with 254 nm UV light, and returned to the original closed form by visible light or thermally. Further reaction revealed that the styryl group substituted phenanthropyran compound **8** underwent the two-step, two-photon photochromic reaction to produce a novel cyclopentaannulated compound **10**.

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