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Synthesis and photochromic properties of novel spiro[indoline-quinoline]oxazine derivatives

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ABSTRACT

A series of novel spirooxazine derivatives containing nitrogen heterocycles have been synthesized and characterized by ^{1}H NMR, ^{13}C NMR, IR and HRMS in this paper, and the photochromic behaviors of the compounds have been studied in different solutions and the compounds were embedded into a poly(-methylmethacrylate) and poly(vinyl butyral) matrix (PMMA, PVB). In solutions, they showed thermochromism and acidichromism. Embedded into polymeric films, the photochromic kinetics of the thermal decoloration of the compounds significantly changed and it was found that the decoloration curves fitted biexponential function. Detailed studies showed that representative compound **1** [1,3,3-trimethyl-6′-piperidino-spiro(indoline-2,3′-[3*H*]-quinolino[2,1-*b*][1,4]oxazine)] exhibited high fatigue resistance in poly(methylmethacrylate) and poly(vinyl butyral) matrix.

1. Introduction

Photochromic materials have attracted a great deal of interest due to their potential application in optical memories and switching devices [1–7]. Up to date, many types of photochromic compounds have been reported. Among them, the spirooxazine (SPO) derivative 1,3-dihydro-1,3,3-trimethyl-spiro(indoline-2,3′-[3*H*]-naphtho[2,1-*b*][1,4]oxazine) was firstly investigated by Fox [8], which turned blue under UV irradiation in toluene solution. Chu and Hovey et al. [9] found the photodegradation rate of the SPO derivatives was very low, then they extended the synthesis of the spirooxazine. With the further study, SPO derivatives exhibit high fatigue resistance, excellent photostability and fast thermal relaxation [10–18]. The photochromic behaviors of these kinds of interesting compounds make them to be used as potential memory devices, optical switches, displays and chemical sensors [19–24]. The durability is a core feature of SPO derivatives while the requirements for each application may be different. Therefore, the methods of stabilizing SPO have been developed. In recent years, we have prepared a number of photochromic SPO compounds, the structure–property relationship has also been studied extensively [25,26].

As part of our continuing research work in photochromic materials, a new class of SPO compounds **1**–**7** were synthesized and characterized fully by means of spectroscopic methods and elemental analysis data. The synthetic route and the structures of the compounds in this work were shown in Scheme 1. In contrast to the SPO derivatives reported by us previously [25,26], nitrogen heterocyclics groups were appended on the SPO skeleton in order to increase the electronic density of the molecular system. and their photochromic behaviors in various media including organic solvents and poly(methylmethacrylate and vinyl butyral) matrix (PMMA, PVB) were studied. These compounds were found to be stable without dulling and fading for prolonged usage. In addition, we also widened the band of the kinds of SPO compounds.

2. Experimental

2.1. General remarks

All chemicals were analytical reagents, which were purchased from Tianjin Reagent Plant, and solvents used were dried and purified by distillation before use. The spectrophotometric grade solvents were used in the spectrophotometric measurements. Spectral measurements were performed in the dark. UV–vis spectra were measured on a Shimadzu UV-2101PC spectrophotometer. ^{1}H NMR spectra were recorded using a Bruker 400 MHz spectrometer with TMS as internal standard in $CDCl_3$. Mass spectra

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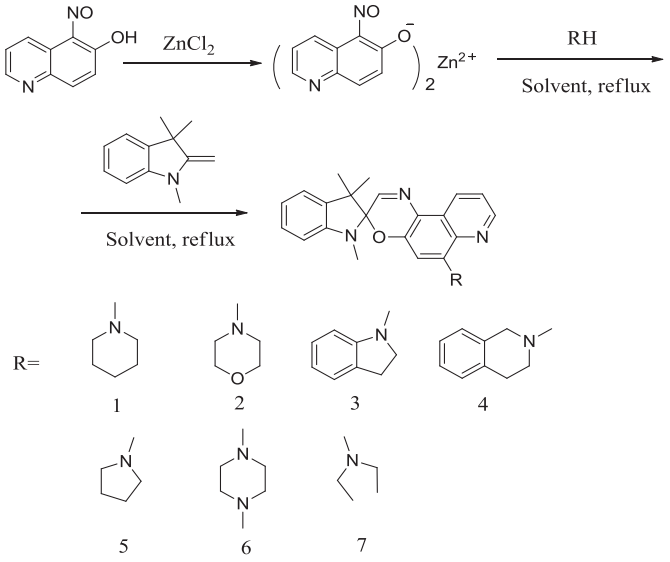

Scheme 1. Synthesis of spiro[indoline-quinoline]oxazine photochromic compounds **1**–**7**.

were measured on a 7070E-HE spectrometer. IR spectra were recorded on a Bio-Rad FTS 135 spectrophotometer using KBr disks and wave numbers were given in cm^{-1}. Melting points were determined with Yanagimoto MP-35 melting point apparatus and were uncorrected. Elemental analysis was performed on a YANACO CHN CORDER MT-3 apparatus.

2.2. General method for synthesis of spirooxazines containing nitrogen heterocycle (entries 1–7)

1.36 g (10 mmol) $ZnCl_2$ in 50 mL aqueous solution was added to the 150 mL mixed solution of tetrahydrofuran and water (1:1 v/v) containing 4.18 g (24 mmol) 5-nitroso-6-hydroxyquinoline while stirring. The reaction was completed after 30 min at room temperature, the raw product of 5-nitroso-6-hydroxyquinoline zinc salt was filtered, then washed with water, and dried under an infrared heat lamp. Yield: 98%.

5-nitroso-6-hydroxyquinoline zinc salt (1.0 mmol) and nitrogen-containing heterocycles compounds (2.8 mmol) were added to 20 mL ethanol. The resulting mixture was stirred for 3 h under reflux. Indoline base (1.8 mmol) in 20 mL ethanol was added to the solution under nitrogen atmosphere, and stirred for additional 16 h at reflux. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (5:1 v/v) as the eluent. The derivatives of spiro[indoline-quinolineoxazine] 1–7 were obtained in modest yields.

*2.2.1. 1,3,3-Trimethyl-6′-piperidino-spiro(indoline-2,3′-[3H]-quinolino[2,1-b][1,4]oxazine) (**1**)*

Primrose yellow solid. Yield 73%. m.p. 200–202 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.83–6.58(9H, m, Ar–H, H-2′), 3.32–3.31(4H, m, 2 × -NCH_2), 2.76(3H, s, NCH_3), 1.85–1.84(4H, m, CH_2), 1.66–1.61(2H, m, CH_2), 1.37(3H, s, CH_3), 1.35(3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ(ppm) 152.8, 147.7, 147.6, 145.9, 144.9, 138.8, 136.0, 130.1, 128.1, 127.1, 121.6, 121.5, 119.9, 117.0, 107.2, 106.1, 99.1, 53.4, 51.7, 29.7, 26.0, 25.5, 24.6, 20.7. IR (KBr, cm^{-1}): 2934, 2852, 2796, 1610, 1582, 1561, 1491, 1446, 1411, 1379. MS (+c ESI) m/z: 413.2 $[M + H]^+$. Anal. Calcd for $C_{26}H_{28}N_4O$: C, 75.70; H, 6.84; N, 13.58. Found: C, 75.38; H, 6.93; N, 13.65.

*2.2.2. 1,3,3-Trimethyl-6′-morpholino-spiro(indoline-2,3′-[3H]-quinolino[2,1-b][1,4]oxazine) (**2**)*

Pink solid. Yield 74.3%. m.p. 216–217 °C. ^{1}H NMR (400 MHZ, $CDCl_3$): δ (ppm) 8.87–6.58(9H, m, ArH, H-2′), 4.02–3.99(4H, m, 2 × OCH_2), 3.43–3.36(4H, m, 2 × -NCH_2), 2.76(3H, s, NCH_3), 1.37(3H, s, CH_3), 1.36(3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.1, 148.3, 147.5, 146.0, 144.9, 138.4, 135.9, 130.4, 128.1, 127.2, 121.8, 121.5, 120.0, 117.5, 107.3, 106.0, 99.2, 67.0, 52.3, 51.7, 29.7, 25.5, 24.6, 20.7. IR (KBr, cm^{-1}): 3025, 2951, 2864, 2818, 1607, 1578, 1557, 1495, 1482, 1445, 1412, 1375, 1304, 1271. HRMS (ESI) m/z: Calcd. $[M + H]^+$ 415.2128, for $C_{25}H_{26}O_2N_4$; Found $[M + H]^+$ 415.2132.

*2.2.3. 1,3,3-Trimethyl-6′-dihydro-indolinyl-spiro(indoline-2,3′-[3H]-quinolino[2,1-b][1,4]oxazine) (**3**)*

Yellow solid. Yield 31.4%. m.p. 222–224 °C. ^{1}H NMR (400 MHZ, $CDCl_3$): δ (ppm) 8.91–6.58(13H, m, ArH, H-2′), 4.30–4.14(2H, m, NCH_2), 3.21(2H, t, $J = 8.2$ Hz, Ar–CH_2), 2.79(3H, s, NCH_3), 1.37(3H, s, CH_3), 1.36(3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 149.0, 148.2, 147.6, 146.4, 145.4, 144.9, 139.1, 135.8, 131.7, 130.2, 128.1, 127.3, 126.6, 124.9, 122.2, 121.5, 120.0, 119.8, 118.6, 111.7, 108.2, 107.3, 99.3, 55.3, 51.9, 29.8, 29.0, 25.5, 20.8. IR (KBr, cm^{-1}): 3046, 2963, 2843, 1682, 1603, 1578, 1553, 1487, 1462, 1416, 1362, 1259, 1163, 1097. MS(+c ESI) m/z: 447.2 $[M + H]^+$. HRMS (ESI) m/z: Calcd. $[M + H]+$ 447.2179, for $C_{29}H_{26}ON_4$; Found $[M + H]+$ 447.2175.

*2.2.4. 1,3,3-Trimethyl-6′-terahydroisoquinolino-spiro(indoline-2,3′-[3H]-quinolino[2,1-b][1,4]oxazine) (**4**)*

Yellow solid. Yield 30%. m.p. 192–194 °C. ^{1}H NMR (400 MHZ, $CDCl_3$): δ (ppm) 8.86v6.58(13H, m, ArH, H-2′), 4.62–4.53(2H, m, NCH2), 3.91–3.79(2H, m, NCH_2), 3.10(2H, t, $J = 5.6$ Hz, Ar-CH_2), 2.77(3H, s, NCH_3), 1.37(3H, s, CH_3), 1.35(3H, s, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 151.1, 147.9, 147.6, 145.9, 145.0, 138.7, 136.0, 134.8, 134.5, 130.2, 128.9, 128.1, 127.2, 126.5, 126.3, 125.9, 121.9, 121.6, 120.0, 117.1, 107.3, 105.9, 99.2, 53.7, 51.7, 50.4, 29.7, 29.1, 25.5, 20.7. IR (KBr, cm^{-1}): 3045, 2967, 2922, 2887, 2817, 2776, 1603, 1582, 1565, 1491, 1446, 1418, 1376, 1302. MS(+c ESI) m/z: 461.2 $[M + H]^+$. Anal. Calcd for $C_{30}H_{28}N_4O$: C, 78.23; H, 6.13; N, 12.16. Found: C, 78.04; H, 5.89; N, 11.89.

*2.2.5. 1,3,3-Trimethyl-6′-pyrrolidino-spiro(indoline-2,3′-[3H]-quinolino[2,1-b][1,4]oxazine) (**5**)*

Red-brown solid. Yield 26%. m.p. 181–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.76–6.23(9H, m, ArH, H-2′), 3.76–3.75(4H, m, 2 × -NCH_2), 2.77(3H, s, NCH_3), 1.99–1.96(4H, m, 2 × CH_2), 1.38(3H, s, CH_3), 1.34(3H, s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 162.3, 148.6, 147.8, 145.9, 145.0, 143.7, 137.3, 136.2, 129.3, 128.0, 127.6, 121.5, 119.7, 113.6, 107.2, 99.2, 98.8, 52.1, 51.5, 29.7, 25.8, 25.7, 25.6, 20.6. IR (KBr, cm^{-1}): 2963, 2868, 1682, 1611, 1565, 1499, 1487, 1449, 1350, 1292, 1225, 1159, 1088. MS(+c ESI) m/z: 399.3 $[M + H]^+$. Anal. Calcd for $C_{25}H_{26}N_4O$: C, 75.35; H, 6.58; N, 14.06. Found: C, 75.12; H, 6.55; N, 14.06.

*2.2.6. 1,3,3-Trimethyl-6′-piperazino-spiro(indoline-2,3′-[3H]-quinolino[2,1-b][1,4]oxazine) (**6**)*

Lavender solid. Yield 35%. m.p. 179–182 °C. ^{1}H NMR (400 MHZ, $CDCl_3$): δ (ppm) 8.85–6.58(9H, m, ArH, H-2′), 3.42–3.36(4H, m, 2 × -NCH_2), 3.23–3.16(4H, m, 2 × -NCH_2), 2.77(3H, s, NCH_3), 1.82(1H, s, NH), 1.37(3H, s, CH_3), 1.35(3H, s, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.9, 148.1, 147.6, 145.9, 144.9, 138.6, 135.9, 130.3, 128.0, 127.2, 121.7, 121.5, 119.9, 117.3, 107.2, 106.2, 99.2, 53.3, 51.7, 46.2, 29.7, 25.5, 20.7. IR (KBr, cm^{-1}): 3329, 2946, 2825, 2740, 1607, 1584, 1558, 1490, 1448, 1414, 1371, 1302, 1256, 1207. HRMS (ESI) m/z: Calcd. $[M + H]^+$ 414.2216, for $C_{25}H_{27}ON_5$; Found $[M + H]^+$ 414.2220.