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Synthesis of functionalized spiropyran and spirooxazine derivatives and their photochromic properties

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Abstract

Three series of functionalized spiropyrans and spirooxazines derivatives were synthesized and their photochromic properties were investigated in particular regard to the fatigue resistance, the lifetime of the colored merocyanine form and the interaction of the colored form molecule. (1) Spiropyrans **5** and spironaphthooxazines **6** having an antioxidant group as a pendant exhibited higher fatigue resistance than that of the parent spiro compounds in solution. In particular, spiropyrans **5** showed higher resistance than parent compound **1** in the presence of an equimolar amount of the corresponding antioxidant. (2) bis-Spironaphthooxazines **8a**–**8i** and **10** connected through a phosphoryl group exhibited higher fatigue resistance and longer lifetime of the colored merocyanine form than those of the parent spirooxazine **7**. (3) Symmetrical bis-spiro photochromic compounds **15** and **16** and unsymmetrical bis-spiro compounds **13**, **14** and **17** were synthesized. The bis-spiro photochromic compounds were found to undergo intramolecular interaction between the colored merocyanine forms.

Keywords: Spiropyran; Spirooxazine; bis-Spiro photochromic compounds; Photochromism; Fatigue resistance

1. Introduction

Among many types of organic photochromic compounds, the chemistry of spiro photochromic compounds has been extensively investigated with special regards to their remarkable properties [1–4]. Particular attentions have been focused on spiropyrans and spirooxazines due to their potential applications to industrial fields [5–22]. These two photochromic compounds can reversibly isomerize from their colorless spiro form (“closed form”) to deeply colored merocyanine form (“open form”) under UV irradiation (Scheme 1). The latter form thermally reverts back to the closed form, resulting in a characteristic color change.

There are several important unsolved problems on this reversible coloration–decoloration process. One of the major problems is the photostability of spiro compounds which undergo photodegradation process known as fatigue phenomenon during the reversible color change. This process has been investigated in terms of the degradation mechanism in solution [23–28], and Guglielmetti and co-workers [26–28] proposed a number of mechanisms for the oxidative degradation processes, which occurred through free radical or singlet oxygen formation. In particular cases, it was shown that the coexistence of a singlet oxygen quencher, 1,4-diazabicyclo[2,2,2]octane (DABCO) [29], or a spin-trapping agent [30–32] exhibits an increase of the fatigue resistance of the photochromic compounds. In our previous report [33], it was found that the introduction of an electron-rich heteroaromatic group into spiropyrans and spirooxazines as a pendant increased their fatigue resistance.

As a further approach to improve the fatigue resistance of photochromic spiro compounds, we report here the synthesis of a series of novel spiropyrans **5a**–**5e** and spirooxazines **6a**–**6d** containing an antioxidant group and the study on their photochromic behaviors. Another approach to the improvement for the fatigue resistance of spirooxazines was carried out by the functionalization of spironaphthooxazines with a phosphoryl group. Aryl or alkyl phosphate compounds was used as antioxidant or photostabilizer in various fields [34–36]. Thus, we synthesized a series of novel bis-spironaphthooxazines **8a**–**8i** and **10** connected through a phosphoryl group and investigated their fatigue resistance.

The second attention was focused on the lifetime of the colored merocyanine form reverting back to the spiro form, namely the decoloration rate of the colored form. It was reported that a photochromic liquid composition containing a phosphine derivative decreased the decoloration rate at

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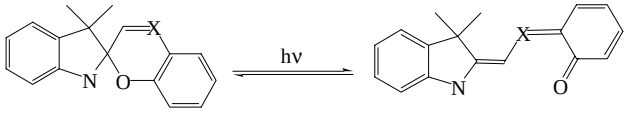


Spiro form
(Colorless closed form)

Merocyanine form
(Colored open form)

Scheme 1. Photochromism of spiropyrans (X = CH) and spirooxazines (X = N).

low temperature [37]. By using the spiropyrans **5a**–**5e** and spirooxazines **8a**–**8i** and **10**, we investigated on the effect of their functionalization on the decoloration rate.

The colored merocyanine form of the spiro compounds has been known to form a dimeric or polymeric aggregate by itself or with the parent spiro form in various media [38–44]. Recently, it has been reported that bis-spiro photochromic compounds, in which two same spiro photochromic groups are linked by a conjugated [45,46] or non-conjugated chain [47–49] showed the variation of the photochromic behaviors. In the case of those two spiro groups linked by non-conjugated chain, the colored merocyanine form showed longer lifetime than that in the corresponding mono-spiro photochromic compound, probably due to the formation of intra- or intermolecular aggregates in the bis-spiro photochromic compound. In order to investigate the photochromic behaviors of various types of the bis-spiro compounds including symmetric and unsymmetric ones, we synthesized a series of symmetrical (spiropyran–spiropyran or spirooxazine–spirooxazine) and unsymmetrical (spiropyran–spirooxazine) bis-spiro compounds **13**–**17** linked by a non-conjugated chain, in addition to the bis-spiro compounds **5d**, **6d**, **8a**–**8i** and **10** which also provide a good model to throw further light on the photochromic behavior of the bis-spiro photochromic compound. These compounds might be also interested to see whether they show a different color from spiropyran and spirooxazine due to the absorptions at the two λ_{max}.

2. Experimental

2.1. General aspects

All melting points were uncorrected. The spectral data were recorded with the following instruments: the IR spectra, Bio-Rad FTS135 spectrophotometer (in KBr pellets); the NMR spectra, Bruker AC-P200 spectrometer using internal TMS for ^{1}H NMR and external 85% H_3PO_4 for ^{31}P NMR; the UV spectra, Shimadzu UV-160A UV-Vis spectrophotometer and Shimadzu UV-2101PC spectrophotometer; the MS spectra, 7070E-HE spectrometer; the ESR spectra, JES-FE1XT spectrometer; and elemental analyses, YANACO CHN CORDER MT-3 analyzer.

The reference compounds **1** [29] and **2** [50], and the starting materials **3** [33], **4** [33] and **7** [50] were synthesized following the procedures in the literatures. Aryl and alkyl dichlorophosphates were synthesized according to the literatures [51–54].

2.2. General procedure for the synthesis of 1′,3′-dihydro-1′-substituted-3′,3′-dimethyl-6-nitro-spiro[2H-indole-2,2′-[3H]-benzopyran]s (5a–5e) and 1,3-dihydro-1-substituted-3,3-dimethyl-spiro[2H-indole-2,3′-[3H]-naphth-[2,1-b][1,4]-oxazine]s (6a–6d)

A solution of 0.38 g (1.0 mmol) of compound **3**, 0.21 g (1.0 mmol) of dicyclohexylcarbodiimide (DCC), 12 mg (0.1 mmol) of 4-dimethylaminopyridine (DMAP) and 0.17 g (1.0 mmol) of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (HOTEMPO) in 20 ml of dry dichloromethane was stirred in the dark at room temperature for 24 h. The precipitated was removed by filtration. The filtrate was washed with an aqueous saturated Na_2CO_3 solution and water successively, dried over anhydrous Na_2SO_4, and concentrated, the residue was submitted to silica gel column chromatography using CH_2Cl_2 as the eluent to give the product 0.38 g (71%) of **5a**, a white solid; mp 193–194 °C; IR: ν = 3050, 2970, 1728, 1608; *m*/*z*: 536, 535, 534; ESR (toluene, X-band, room temperature): triplet (1:1:1), g = 2.007, a = 15.34 G; anal. cacld. for $C_{30}H_{36}N_3O_6$ (formula weight: 534.63): C 67.40, H 6.79, N 7.86; found: C 67.50, H 6.74, N 7.63. Spiropyran **5b**: a pale yellow solid, 61%; mp 146–147 °C; IR: ν = 3040, 2930, 2850, 1665, 1602; *m*/*z*: 461, 446; ^{1}H NMR ($CDCl_3$): δ = 1.16 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.40–1.89 (m, 16H, $2CH_2$, $4CH_3$), 2.64–2.81 (m, 2H, CH_2), 3.20 (m, 1H, CH), 3.46–3.80 (m, 5H, CH_3, CH_2), 5.83 (d, J = 10.8 Hz, 1H, –CH=), 6.60–7.24 (m, 6H, ArH), 7.97–8.03 (m, 2H, ArH); anal. cacld. for $C_{31}H_{39}N_3O_5$ (formula weight: 533.67): C 69.77, H 7.37, N 7.87; found: C 70.02, H 6.94, N 7.91. Spiropyran **5c**: a pale yellow solid, 58%; mp 191–192 °C; IR: ν = 3195, 3060, 2970, 2934, 1725, 1611; *m*/*z*: 521, 520, 519; ^{1}H NMR ($CDCl_3$): δ = 1.13 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.38–1.40 (m, 12H, $4CH_3$), 1.45–1.86 (m, 4H, $2CH_2$), 2.41–2.77 (m, 2H, CH_2), 3.41–3.62 (m, 3H, CH, CH_2), 5.06 (br, 1H, NH), 5.84 (d, J = 9.8 Hz, 1H, –CH=), 6.55–7.21 (m, 6H, ArH), 7.98–8.01 (m, 2H, ArH); anal. cacld. for $C_{30}H_{37}N_3O_5$ (formula weight: 519.64): C 69.34, H 7.18, N 8.09; found: C 69.48, H 7.05, N 8.22. bis-Spiropyran **5d**: a white solid, 46%; mp 138–139 °C; IR: ν = 3050, 2931, 2854, 1740, 1680, 1660, 1610; *m*/*z*: 456, 363, 335; ^{1}H NMR ($CDCl_3$): δ = 1.18–1.28 (m, 12H, $4CH_3$), 1.64 (s, 6H, $2CH_3$), 2.77–2.99 (m, 4H, $2CH_2$), 3.59–3.80 (m, 4H, CH_2), 5.93 (d, J = 10.8 Hz, 2H, –CH=), 6.67–7.26 (m, 20H, ArH), 7.97–8.05 (m, 4H, ArH); anal. cacld. for $C_{57}H_{52}N_4O_{10}$ (formula weight: 953.06): C 71.83, H 5.50, N 5.88; found: C 71.92, H 5.47, N 5.59. Spiropyran **5e**: a white solid, 43%; mp 150–151 °C; IR: ν = 3050, 2930, 2850, 1660, 1572; *m*/*z*: 461, 446; ^{1}H NMR ($CDCl_3$): δ = 1.17, 1.27 (2s, 6H, $2CH_3$), 1.66–1.90 (m, 18H, $6CH_3$), 2.75 (m, 2H, CH_2), 3.64 (m, 5H, CH_2, CH_3), 5.85 (d, J = 10.8 Hz, 1H,

–CH=), 6.60–7.33 (m, 8H, ArH), 7.98–8.04 (m, 2H, ArH); anal. cacld. for $C_{36}H_{42}N_2O_5$ (formula weight: 582.74): C 74.20, H 7.26, N 4.81; found: C 73.92, H 7.44, N 4.58.

Spironaphthooxazine **6a**: A pale green solid (0.39 g, 71%), prepared from 0.39 g (1.0 mmol) of **4** and 0.17 g (1.0 mmol) of HOTEMPO; mp 162–163 °C; IR: ν = 3050, 2930, 2851, 1700, 1655, 1605; *m/z*: 542, 541, 540; ESR (toluene, X-band, room temperature): triplet (1:1:1), g = 2.005, a = 15.33 G; anal. cacld. for $C_{33}H_{38}N_3O_4$ (formula weight: 540.68): C 73.31, H 7.08, N 7.77; found: C 73.55, H 7.01, N 7.73. Spironaphthooxazine **6b**: a pale green solid, 52%; mp 139 °C; IR: ν = 3065, 2940, 2860, 1705, 1628, 1605; *m/z*: 492, 369; ^{1}H NMR ($CDCl_3$): δ = 1.14–1.24 (m, 12H, $4CH_3$), 1.28 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.54–1.69 (m, 2H, CH_2), 1.87–1.93 (m, 2H, CH_2), 3.21–3.54 (m, 3H, CH, CH_2), 3.88–4.22 (m, 2H, CH_2), 4.48 (s, 3H, NCH_3), 6.61 (d, J = 8.0 Hz, 1H, ArH), 6.81–7.47 (m, 8H, ArH, and –CH=), 7.67 (d, J = 8.0 Hz, 1H, ArH), 7.76 (d, J = 8.0 Hz, 1H, ArH); anal. cacld. for $C_{34}H_{41}N_3O_3$ (formula weight: 539.71): C 75.6, H 7.66, N 7.79; found: C 75.39, H 7.69, N 7.88. Spironaphthooxazine **6c**: a pale green solid, 48%; mp 147 °C; IR: ν = 3215, 3055, 2960, 2840, 1710, 1624, 1609; *m/z*: 369, 342; ^{1}H NMR ($CDCl_3$): δ = 1.13–1.26 (m, 12H, $4CH_3$), 1.29 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.57–1.88 (m, 4H, $2CH_2$), 2.73–3.01 (m, 2H, CH_2), 3.31 (m, 1H, CH), 3.83–4.20 (m, 2H, CH_2), 5.07 (br, 1H, NH), 6.59 (d, J = 8.0 Hz, 1H, ArH), 6.80–7.45 (m, 8H, ArH and –CH=), 7.67 (d, J = 8.0 Hz, 1H, ArH), 7.77 (d, J = 8.0 Hz, 1H, ArH); anal. cacld. for $C_{33}H_{39}N_3O_3$ (formula weight: 525.69): C 75.40, H 7.48, N 7.93; found: C 75.59, H 7.29, N 8.01. bis-Spironaphthooxazine **6d**: a milky-white solid, 39%; mp 163–166 °C; IR: ν = 3050, 2965, 2870, 1755, 1625, 1605; *m/z*: 369, 357; ^{1}H NMR ($CDCl_3$): δ = 1.28–1.35 (m, 12H, $4CH_3$), 1.61 (s, 6H, $2CH_3$), 2.84–3.08 (m, 4H, $2CH_2$), 3.63–3.91 (m, 4H, $2CH_2$), 6.66–7.20 (m, 16H, ArH), 7.40–7.82 (m, 12H, ArH and –CH=), 8.59 (d, J = 8.1 Hz, 2H, ArH); anal. cacld. for $C_{63}H_{56}N_4O_6$ (formula weight: 965.11): C 78.40, H 5.85, N 5.81; found: C 78.11, H 5.64, N 5.49.

2.3. General procedure for the synthesis of bis-spironaphthooxazines *8a–8i*

Under nitrogen atmosphere and ice-bath cooling to the solution of 0.35 g (1.0 mmol) of compound **7**, 6 mg (0.05 mmol) of DMAP and 0.5 ml (3.5 mmol) of triethylamine in 10 ml of dry toluene was dropwise added a solution of 0.07 g (0.5 mmol) of ethyl dichlorophosphate in 5 ml of dry toluene with stirring in the dark. The reaction mixture was stirred at room temperature for 24 h, then washed with diluted hydrochloric acid and water, successively, and dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was submitted to silica gel column chromatography using acetone/petroleum ether (1:4, v/v) as the eluent to give **8a** (0.35 g, 90%), a pale blue solid; mp 172–174 °C; IR: ν = 3032, 2959, 2928, 2860, 1627, 1604; *m/z*: 480, 344; ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 12H, $4CH_3$), 1.45 (t, J = 7.3 Hz, 3H, CH_3), 2.73 (s, 6H, $2NCH_3$), 4.45 (quintuplet, J = 7.3 Hz, 2H, OCH_2), 6.56 (d, J = 8.4 Hz, 2H, ArH), 6.84–7.21 (m, 8H, ArH), 7.35 (d, J = 9.4 Hz, 2H, ArH), 7.59–7.74 (m, 6H, 4ArH and 2CH=), 8.42 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): δ = −12.38; anal. cacld. for $C_{46}H_{43}N_4O_6P$ (formula weight: 778.804): C 70.94, H 5.56, N 7.19; found: C 70.69, H 5.32, N 7.28. bis-Spironaphthooxazine **8b**: a pale blue solid, 91%; mp 130 °C; IR: ν = 3056, 2961, 2931, 2871, 1622, 1606; *m/z*: 345, 344; ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 12H, $4CH_3$), 2.74 (s, 6H, $2NCH_3$), 6.56 (d, J = 7.7 Hz, 2H, ArH), 6.89–7.21 (m, 9H, ArH), 7.30–7.37 (m, 6H, ArH), 7.60–7.75 (m, 6H, 4ArH and 2CH=), 8.47 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): δ = −17.43; anal. cacld. for $C_{50}H_{43}N_4O_6P$ (formula weight: 826.89): C 72.63, H 5.24, N 6.78; found: C 72.41, H 5.0, N 6.85. bis-Spironaphthooxazine **8c**: a pale blue solid, 70%; mp 119–120 °C; IR: ν = 3050, 2960, 2862, 1622, 1606; *m/z*: 558, 543, 329; ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 12H, $4CH_3$), 2.73 (s, 6H, $2NCH_3$), 3.78 (s, 3H, OCH_3), 6.56 (d, J = 7.6 Hz, 2H, ArH), 6.84–7.37 (m, 14H, ArH), 7.60–7.74 (m, 6H, 4ArH and 2CH=), 8.46 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): δ = −17.63; anal. cacld. for $C_{51}H_{45}N_4O_7P$ (formula weight: 856.92): C 71.48, H 5.29, N 6.54; found: C 71.66, H 5.42, N 6.35. bis-Spironaphthooxazine **8d**: a pale blue solid, 71%; mp 125–126 °C; IR: ν = 3052, 2960, 2870, 1623, 1606; *m/z*: 345, 344, 329; ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 12H, $4CH_3$), 2.33 (s, 3H, CH_3), 2.74 (s, 6H, $2NCH_3$), 6.56 (d, J = 7.7 Hz, 2H, ArH), 6.76–7.24 (m, 11H, ArH), 7.33 (s, 1H, ArH), 7.38 (s, 1H, ArH), 7.60–7.78 (m, 7H, 5ArH and 2CH=), 8.47 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): δ = −18.17; anal. cacld. for $C_{51}H_{45}N_4O_6P$ (formula weight: 840.92): C 72.84, H 5.39, N 6.66; found: C 73.08, H 5.22, N 6.53. bis-Spironaphthooxazine **8e**: a pale blue solid, 81%; mp 117–119 °C; IR: ν = 3052, 2960, 2870, 1623, 1606; *m/z*: 345, 344, 329; ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 12H, $4CH_3$), 2.35 (s, 3H, CH_3), 2.74 (s, 6H, $2NCH_3$), 6.57 (d, J = 7.8 Hz, 2H, ArH), 6.85–7.38 (m, 14H, ArH), 7.61–7.75 (m, 6H, 4ArH and 2CH=), 8.47 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): δ = −17.96; anal. cacld. for $C_{51}H_{45}N_4O_6P$ (formula weight: 840.92): C 72.84, H 5.39, N 6.66; found: C 72.88, H 5.22, N 6.57. bis-Spironaphthooxazine **8f**: a pale blue solid, 73%; mp 122–124 °C; IR: ν = 3052, 2960, 2870, 1623, 1606; *m/z*: 345, 344, 329; ^{1}H NMR ($CDCl_3$): δ = 1.34 (s, 12H, $4CH_3$), 2.30 (s, 6H, $2CH_3$), 2.75 (s, 6H, $2NCH_3$), 6.57 (d, J = 8.4 Hz, 2H, ArH), 6.89–7.21 (m, 11H, ArH), 7.36 (d, J = 8.4 Hz, 2H, ArH), 7.61–7.75 (m, 6H, 4ArH and 2CH=), 8.48 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): δ = −18.05; anal. cacld. for $C_{52}H_{47}N_4O_6P$ (formula weight: 854.97): C 73.05, H 5.54, N 6.55; found: C 72.93, H 5.49, N 6.68. bis-Spironaphthooxazine **8g**: a pale blue solid, 91%; mp 119–120 °C; IR: ν = 3050, 2959, 2925, 2870, 1623, 1607; *m/z*: 344, 329; ^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 12H, $4CH_3$), 2.74 (s, 6H, $2NCH_3$), 6.56 (d, J = 7.7 Hz, 2H, ArH), 6.89–7.31 (m, 14H, ArH), 7.60–7.76 (m, 6H, 4ArH and 2CH=), 8.43 (s, 2H, ArH); ^{31}P NMR

($CDCl_3$): $\delta = -18.57$; anal. cacld. for $C_{50}H_{42}ClN_4O_6P$ (formula weight: 861.33): C 69.72, H 4.91, N 6.51; found: C 70.01, H 4.66, N 6.32. bis-Spironaphthooxazine **8h**: a pale blue solid, 78%; mp 134–135 °C; IR: $\nu = 3050$, 2959, 2870, 1623, 1607; *m/z*: 344, 329; ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 12H, $4CH_3$), 2.73 (s, 6H, $2NCH_3$), 6.552 (d, $J = 7.8$ Hz, 2H, ArH), 6.84–7.20 (m, 8H, ArH), 7.33–7.70 (m, 11H, 9ArH, 2CH=), 8.47 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): $\delta = -18.41$; anal. cacld. for $C_{50}H_{41}Cl_2N_4O_6P$ (formula weight: 895.744): C 67.04, H 4.61, N 6.26; found: C 66.93, H 4.52, N 6.12. bis-Spironaphthooxazine **8i**: a pale blue solid, 82%; mp 117–118 °C; IR: $\nu = 3044$, 2953, 2860, 1702, 1610; *m/z*: 345, 344, 329; ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (s, 6H, $2CH_3$), 1.31 (s, 6H, $2CH_3$), 2.71 (s, 6H, $2NCH_3$), 6.54 (d, $J = 7.6$ Hz, 2H, ArH), 6.89 (q, $J = 7.2$ Hz, 4H, ArH), 7.06 (d, $J = 7.2$ Hz, 2H, ArH), 7.18 (d, $J = 7.6$ Hz, 2H, ArH), 7.33 (d, $J = 8.2$ Hz, 2H, ArH), 7.51–7.68 (m, 9H, 7ArH, 2CH=), 8.10 (q, $J = 6.7$ Hz, 2H, ArH), 8.37 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): $\delta = 10.36$; anal. cacld. for $C_{50}H_{43}N_4O_5P$ (formula weight: 810.89): C 74.06, H 5.34, N 6.91; found: C 73.98, H 5.21, N 6.72.

2.4. Synthesis of bis-spironaphthooxazine **10**

Under nitrogen atmosphere and ice-bath cooling to the solution of 0.69 g (2.0 mmol) of compound **7**, 12 mg (0.1 mmol) of DMAP and 1.0 ml of triethylamine in 25 ml of dry toluene was dropwise added a solution of 0.18 g (1.0 mmol) of dichlorophenylphosphine in 10 ml of dry toluene with stirring in the dark. The reaction mixture was stirred at room temperature for 24 h, then 1.0 g of sulfur was added. The mixture was stirred for another 5 h at 45–50 °C. A solid was removed by filtration, and the filtrate was washed with diluted hydrochloric acid and water, successively, and dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was submitted to silica gel column chromatography using acetone/petroleum ether (1:4, v/v) as the eluent. A pale blue solid product **10** (0.60 g, 82%) was obtained; mp 140 °C; IR: $\nu = 3054$, 2960, 2927, 2865, 1620, 1608; ^{1}H NMR ($CDCl_3$): $\delta = 1.32$ (s, 12H, $4CH_3$), 2.72 (s, 6H, $2NCH_3$), 6.55 (d, $J = 7.8$ Hz, 2H, ArH), 6.87–7.34 (m, 10H, ArH), 7.56–7.69 (m, 9H, 7ArH, 2CH=), 8.32 (q, $J = 7.0$ Hz, 2H, ArH), 8.39 (s, 2H, ArH); ^{31}P NMR ($CDCl_3$): $\delta = 82.58$; anal. cacld. for $C_{50}H_{43}N_4O_4PS$ (formula weight: 826.96): C 72.62, H 5.24, N 6.78; found: C 72.39, H 5.19, N 6.92.

2.5. Synthesis of spironaphthopyran **11**

To a solution of 3.31 g (10.0 mmol) of 1-(2′-hydroxyethyl)-2,3,3-trimethyl-indoleninium iodide [48] in 15 ml of absolute ethanol were added 1.0 ml (10.0 mmol) of piperidine and then 1.72 g (10.0 mmol) of 2-hydroxy-1-naphthaldehyde with stirring. The mixture was heated at reflux for 5 h and cooled to precipitate a solid. The solid was separated by filtration, wished with cold acetone and re-crystallized from acetone to give compound **7** as a white solid (1.57 g, 44%); mp 167–168 °C. IR: $\nu = 3430$, 3060, 2940, 2860, 1635, 1605; ^{1}HNMR ($CDCl_3$): $\delta = 1.21$ (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 3.34–3.42 (m, 2H, CH_2), 3.67–3.74 (m, 2H, CH_2), 5.78 (d, 1H, $J = 10.8$ Hz, C–CH=), 6.61–7.87 (m, 11H, ArH, one =CH–Ar); anal. cacld. for $C_{24}H_{23}NO_2$ (formula weight: 357.44): C 80.64, H 6.49, N 3.92; found: C 80.33, H 6.39, N 3.79.

2.6. Synthesis of spiropyran **12**

To a cold solution of 0.76 g (2.0 mmol) of compound **3** in 20 ml of dry DMF were added 0.29 g (2.5 mmol) of *N*-hydroxysuccinimide (NHS) and 0.52 g (2.5 mmol) of DCC. The solution was stirred at room temperature in the dark for 24 h. The generated solid dicyclohexylurea (DCU) was filtered off, and the filtrate was evaporated under reduced pressure. The residue was dissolved in ethyl acetate, and the solution was washed with saturated aqueous Na_2CO_3 and water, successively, and dried over $MgSO_4$. To the solution was added petroleum ether to precipitate the intermediate succinimide derivative as a pale yellow solid (0.9 g, 94.1%).

A solution of 1 mol l^{-1} $NaHCO_3$ solution (4 ml) containing 0.13 g (1.0 mmol) of 6-aminocaproic acid was added dropwise to a solution of 0.48 g (1.0 mmol) of the succinimide derivative in 3 ml of DMF. The mixture was stirred at room temperature in the dark for 6 h. The solvent was evaporated under reduced pressure. To the residue was added 10 ml of 10% aqueous citric acid solution to give a pale pink precipitate. The precipitate was washed with cold water and dried in vacuo to give compound **12** as a pink solid (0.48 g, 97.4%); mp. 80–81 °C; IR: $\nu = 3300$, 3060, 2930, 2860, 1725, 1675, 1615; ^{1}H NMR ($CDCl_3$): $\delta = 1.15$ (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.32–1.66 (m, 6H, $3CH_2$), 2.20–2.60 (m, 4H, $2CH_2$), 3.50–3.68 (m, 4H, $2CH_2$), 5.72 (br, 1H, NH), 5.89 (d, 1H, $J = 10.8$ Hz, C–CH=), 6.65–7.25 (m, 6H, ArH, one =CH–Ar), 8.00–8.15 (m, 2H, ArH); anal. cacld. for $C_{27}H_{31}N_3O_6$ (formula weight: 493.55): C 65.71, H 6.33, N 8.51; found: C 65.49, H 6.25, N 8.60.

2.7. General procedure for the synthesis of bis-spiro compounds **13–17**

Under nitrogen atmosphere, a solution of 0.38 g (1.0 mmol) of compound **3**, 0.21 g (1.0 mmol) of DCC and 12 mg (0.1 mmol) of DMAP in 20 ml of dry dichloromethylene was stirred in the dark at 0–5 °C for 2 h. To the solution 0.35 g (1.0 mmol) of compound **7** in 10 ml of dry dichloromethylene was added dropwise, and stirred in the dark at room temperature for 24 h. After removing the solid by filtration, the filtrate was washed by saturated Na_2CO_3 solution and water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was applied on silica gel column using CH_2Cl_2 as the eluent to give compound **13** (0.45 g, 64%), a pale yellow solid; mp 182–184 °C;

IR: ν = 3054, 2962, 2869, 1752, 1654, 1608; *m/z*: 707, 706, 691; ^{1}H NMR ($CDCl_3$): δ = 1.20–1.35 (4s, 12H, $4CH_3$), 2.75 (s, 3H, CH_3), 2.96 (q, J = 6.3 Hz, 2H, CH_2), 3.75 (q, J = 6.3 Hz, 2H, CH_2), 5.94 (d, J = 10.8 Hz, 1H, –CH=C), 6.55–7.33 (m, 13H, ArH, –CH=), 7.60 (s, 1H, ArH), 7.69–7.79 (m, 2H, ArH), 8.00–8.19 (m, 2H, ArH); anal. cacld. for $C_{43}H_{38}N_4O_6$ (formula weight: 706.80): C 73.07, H 5.42, N 7.93; found: C 73.22, H 5.44, N 7.68. bis-Spiro compound **14**: a reddish brown solid, 68%; mp 153–154 °C; IR: ν = 3395, 3320, 3041, 2921, 2850, 1754, 1641, 1605; *m/z*: 344, 329; ^{1}H NMR ($CDCl_3$): δ = 1.11–1.32 (4s, 12H, $4CH_3$), 1.58–1.95 (m, 6H, $3CH_2$), 2.51–2.61 (m, 2H, CH_2), 2.71 (s, 3H, NCH_3), 3.11–3.24 (m, 2H, CH_2), 3.37–3.51 (m, 2H, CH_2), 3.63–3.77 (m, 2H, CH_2), 5.54 (br, 1H, NH), 5.80 (d, J = 10.4 Hz, 1H, –CH=C), 6.54–7.20 (m, 12H, ArH, –CH=), 7.60–7.74 (m, 3H), 7.95 (s, 2H, ArH), 8.17 (s, 1H, ArH); anal. cacld. for $C_{49}H_{49}N_5O_7$ (formula weight: 819.92): C 71.77, H 6.02, N 8.54; found: C 71.53, H 5.84, N 8.47. bis-Spironaphthooxazine **15**: a pale gray solid, 58%; mp 143 °C; IR: ν = 3050, 2960, 2869, 1755, 1605; *m/z*: 713, 712, 697; ^{1}H NMR ($CDCl_3$): δ = 1.28–1.37 (m, 12H, $4CH_3$), 2.68 (s, 3H, NCH_3), 2.97 (m, 2H, CH_2), 3.70 (m, 2H, CH_2), 6.48–7.79 (m, 19H, ArH, –CH=), 8.15 (d, J = 1.8 Hz, 1H, ArH), 8.55 (d, J = 9.0 Hz, 1H, ArH); anal. cacld. for $C_{46}H_{40}N_4O_4$ (formula weight: 712.86): C 77.51, H 5.66, N 7.86; found: C 77.40, H 5.65, N 8.00. bis-Spiropyran **16**: a pale pink solid, 40%; mp 185–186 °C; IR: ν = 3050, 2955, 1720, 1610; *m/z*: 689, 643, 380, 363, 357; ^{1}H NMR ($CDCl_3$): δ = 1.20–1.29 (m, 12H, $4CH_3$), 2.50–2.61 (m, 2H, CH_2), 3.44–3.82 (m, 6H, $3CH_2$), 5.76–5.94 (m, 2H, –CH=), 6.60–7.90 (m, 17H, ArH, –CH=), 8.01–8.11 (m, 2H, ArH); anal. cacld. for $C_{45}H_{41}N_3O_6$ (formula weight: 719.80): C 75.08, H 5.74, N 5.84; found: C 75.16, H 5.58, N 5.91. bis-Spiro compound **17**: a pale pink solid, 51%; mp 202 °C; IR: ν = 3050, 2962, 2862, 1750, 1630, 1605; *m/z*: 386, 369, 357, 342; ^{1}H NMR ($CDCl_3$): δ = 1.25 (s, 6H, $2CH_3$), 1.39 (s, 6H, $2CH_3$), 2.90–3.15 (m, 4H, $2CH_2$), 3.70–4.00 (m, 4H, $2CH_2$), 5.97 (d, J = 10.8 Hz, 1H, –CH=C), 6.65–8.36 (m, 22H, ArH, –CH=); anal. cacld. for $C_{48}H_{43}N_3O_4$ (formula weight: 725.89): C 79.42, H 5.97, N 5.79; found: C 79.53, H 6.02, N 5.99.

2.8. The absorption spectra of spiro compounds in various solvents before and after UV irradiation

Solutions of the reference spiro compounds **1**, **2** and **7** and the newly synthesized spiro compounds **5a**–**5e**, **6a**–**6d**, **8a**–**8i**, **10** and **13**–**17** of the concentration of 1×10^{-5} to

Table 1
The λ_{max} of spiro photochromic compounds in the closed spiro form in various solvents

Compound	λ_{max} (nm), solvent (E value)[a]			
	Methanol (55.5)	Acetonitrile (46.0)	Acetone (42.2)	Cyclohexane (31.2)
1	237.5, 271, 339.5	236.5, 270, 339	341	238, 274, 339.5
5a	239.5, 268.5, 341	239, 270.5, 340.5	342	238, 274, 339.5
5b	238.5, 272, 342.5	240, 272.5, 343.5	341	239.5, 270.5, 340.5
5c	239, 271.5, 341	237.5, 273, 343	340	238.5, 271, 342.5
5d	242, 273.5, 344.5	241.5, 272, 343	346	240, 272, 341.5
5e	241.5, 272, 341.5	240.5, 271.5, 342	343.5	240.5, 271.5, 341
2	241, 269.5, 342.5	240.5, 271, 340.5	346	240.5, 270.5, 340.5
6a	239.5, 271, 341.5	238.5, 270.5, 340	346	240, 271, 340.5
6b	240.5, 270, 340.5	239.5, 272, 341.5	339.5	240.5, 270.5, 341
6c	241, 271.5, 343	241, 271.5, 343	341.5	239, 271.5, 341.5
6d	243.5, 274, 347	240.5, 272.5, 343.5	341	240.5, 273, 342.5
8a	240.5, 271.5, 341.5	238.5, 271.5, 338.5	343.5	239.5, 270, 337.5
8b	241, 271.5. 338.5	240, 270.5, 338	335.5	240, 270.5, 339.5
8c	239.5, 270.5, 342	241, 271, 339	334.5	239, 272.5, 342
8d	240, 272, 339.5	241.5, 270.5, 340	335.5	240.5, 273, 341.5
8e	241.5, 271.5, 341.5	242, 271.5, 339.5	335.5	240, 273.5, 343
8f	242, 272.5, 342	241, 272, 340.5	335	238.5, 272.5, 340.5
8g	240.5, 271.5, 341.5	242.5, 273.5, 338.5	337.5	239, 271.5, 343.5
8h	238.5, 271, 342.5	242.5, 271, 340.5	338.5	243.5, 273.5, 344
8i	243.5, 272.5, 339.5	240.5, 271.5, 341.5	334.5	241, 2372, 340.5
10	245.5, 275, 345.5	242.5, 274.5, 347.5	339.5	242.5, 274, 345.5
7	240.5, 270.5, 343	239.5, 271.5, 340.5	345	240.5, 271, 340.5
1 + **7** (1:1)	238, 271.5, 337.5	239.5, 270, 339.5	343	240, 270.5, 340
13	238.5, 337.5	240.5, 273, 338.5	337	239, 271.5, 340.5
14	237, 271.5, 342.5	238.5, 272, 342	343	240, 272.5, 341.5
15	240, 270.5, 342.5	240.5, 273, 339.5	346	239.5, 271.5, 340
16	238, 272.5, 343.5	240, 271.5, 343.5	346	241.5, 272, 341
17	241, 340.5	241, 270.5, 341.5	346	140.5, 271.5, 341

[a] Dimroth's solvent polarity parameters E were taken from [57].

Table 2
The λ_{max} of spiro photochromic compounds containing an antioxidant pendant after UV irradiation (opened merocyanine form)

Compound	λ_{max}(nm), solvent (E value)[a]			
	Methanol (55.5)	Acetonitrile (46.0)	Acetone (42.2)	Cyclohexane (31.2)
1	524.5	555	570	580.5, 612
5a	536.5	564.5	557	502
5b	538	566.5	573	581.5
5c	537.5	565	575	586
5d	547	561	567	588.5
5e	533.5	567.5	574.5	583.5
2	611	600.5	584	578.5
6a	619	588	581.5	567
6b	607.5	594.5	584	577
6c	605	596	585	580
6d	605	601.5	598.5	580

[a] Dimroth's solvent polarity parameters E were taken from [57].

1×10^{-4} mol l^{-1} in various solvents (methanol, acetonitrile, acetone and cyclohexane) were prepared. The UV spectrum of each solution was recorded on a Shimadzu UV-160A UV-Vis spectrophotometer. The λ_{max} of the compounds are listed in Table 1.

The same solutions were irradiated with a 400 W high-pressure mercury lamp with Pyrex housing for 30 s, and the spectra were recorded immediately after the irradiation. The λ_{max} of the merocyanine forms thus obtained are listed in Tables 2 and 3.

Table 3
The λ_{max} of bis-spiro photochromic compounds after UV irradiation (opened merocyanine form)

Compound	λ_{max}(nm), solvent (E value)[a]			
	Methanol (55.5)	Acetonitrile (46.0)	Acetone (42.2)	Cyclohexane (31.2)
1	524.5	555	570	580.5, 612
5e	533.5	567.5	574.5	583.5
16	556	569.5	576	584.5
2	611	600.5	584	578.5
7	605	598.5	585	579.5
6d	605	601.5	598.5	580
15	602.5	598	600.5	573.5
8a	604.5	602	602	589
8b	603.5	601.5	601	589.5
8c	603	601	600.5	586.5
8d	603	601.5	600.5	588.5
8e	604	602.5	601.5	587.5
8f	604.5	602	602.5	589
8g	603.5	601	600.5	588
8h	603	601.5	601.5	587
8i	604	602	601.5	586.5
10	606.5	601.5	602	585.5
1 + **7** (1:1)	564 (br)	569.5	571	581
13	557, 602.5	568.5 (br)	577.5 (br)	579
14	560, 601.5	566.5 (br)	571.5 (br)	581.5
17	605.5	601	598	578

[a] Dimroth's solvent polarity parameters E were taken from [57].

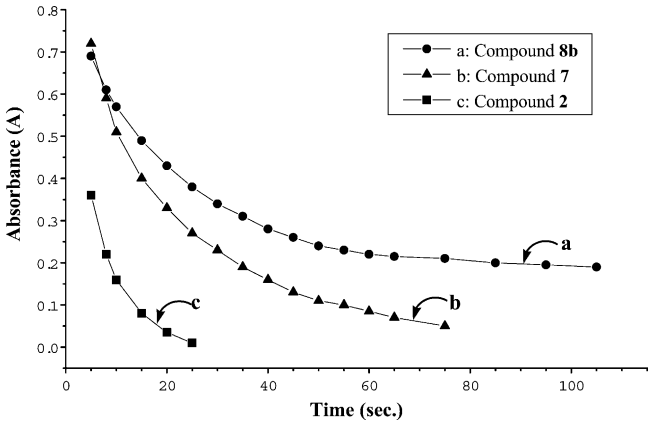


Fig. 1. The absorbance (A) change at the λ_{max} of: (a) compound **8b** (λ_{max} = 589.5 nm, $c = 5.0 \times 10^{-4}$ mol l^{-1}); (b) compound **7** (λ_{max} = 579.5 nm, $c = 1.0 \times 10^{-3}$ mol l^{-1}); (c) compound **2** (λ_{max} = 578.5 nm, $c = 1.0 \times 10^{-3}$ mol l^{-1}) in cyclohexane solution during the decoloration process at room temperature.

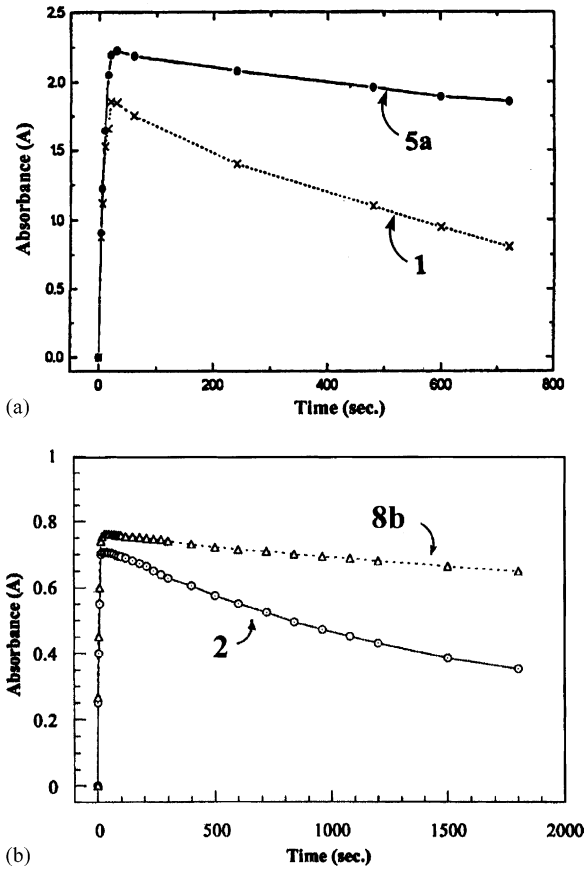


Fig. 2. (a) The absorbance (A) change at the λ_{max} of compounds **1** (λ_{max} = 580.5 nm, $c = 1.0 \times 10^{-4}$ mol l^{-1}) and **5a** (λ_{max} = 602 nm, $c = 1.0 \times 10^{-4}$ mol l^{-1}) in cyclohexane solution under continuous UV irradiation. (b) The absorbance (A) change at the λ_{max} of compounds **2** (λ_{max} = 578.5 nm, $c = 1.0 \times 10^{-3}$ mol l^{-1}) and **8b** (λ_{max} = 589.5 nm, $c = 1.0 \times 10^{-4}$ mol l^{-1}) in cyclohexane solution under continuous UV irradiation.

Table 4
The parameter ($t_{A_0/2}$) of the spiro compounds in cyclohexane solution

Compound	$t_{A_0/2}$[a] (min)
1	12
2	50
5a	690
5b	570
5c	540
5d	300
5e	360
8a	150
8b	170
8c	180
8d	165
8e	175
8f	160
8g	155
8h	150
8i	135
10	120

[a] $t_{A_0/2}$ is the time in minute required to decrease the initial absorbance (A_0) of the merocyanine form to the half value ($A_0/2$) at the λ_{max}.

2.9. The decoloration process of the colored merocyanine form of spirooxazines *2*, *7*, *8a–8i* and *10* in cyclohexane

Solutions of compounds **2** (1.0×10^{-3} mol l^{-1}), **7** (1.0×10^{-3} mol l^{-1}), **8a–8i** and **10** (5.0×10^{-4} mol l^{-1}) in cyclohexane were prepared. The absorbance (A) of each solution at its λ_{max} was recorded immediately after 30 s irradiation with a 400 W high-pressure mercury lamp. The absorbances (A) at the same λ_{max} for a given compound in different time were plotted. A typical example of the plot made for compounds **2**, **7** and **8b** is illustrated in Fig. 1.

2.10. The parameter $t_{A_0/2}$ for the fatigue resistance of spiro compounds in the colored merocyanine form in cyclohexane

Solutions of the reference compounds **1** and **2** (1.0×10^{-3} mol l^{-1}), and the compounds **5a–5e**, **8a–8i** and **10** (5.0×10^{-4} mol l^{-1}) in cyclohexane were prepared. Each solution was divided into 30 parts, and the parts were irradiated at the same time with a 400 W high-pressure mercury lamp. The absorbances (A) at λ_{max} of a given compound in different irradiation time were recorded on a spectrophotometer immediately after irradiation. A plot of the absorbance against the irradiation time was made to give Fig. 2a for **1** and **5a** and Fig. 2b for **2** and **8b**. The parameter $t_{A_0/2}$ obtained from the plot is defined as the time in minute required to decrease the initial absorbance (A_0) at the λ_{max} of the merocyanine form to the half value ($A_0/2$). The parameters obtained for **5a–5e**, **8a–8i** and **10** are listed in Table 4 in comparison with those of the reference compounds **1** and **2**.

2.11. Evaluation of the fatigue resistance of spiro compounds in methanol

Solutions of the reference compounds **1** and **2** (1.0×10^{-3} mol l^{-1}), and the compounds **5a–5e**, **8a–8i** and **10** (5.0×10^{-4} mol l^{-1}) in methanol were prepared. Solutions of compound **1**, the mixture of compound **1** and an antioxidant (molar ratio = 1:1), and compound **5a** in methanol ($5.0 \times$

Table 5
Decrease of the absorbance (A) of compound **1**, the mixture of compound **1** and an antioxidant (1:1), and the spiro chromic compounds **2**, **5**, **8** and **10** in methanol solution at every repeated cycle of photocoloration and thermal decoloration

Entry	Compounds (λ_{max}, nm)	Absorbance (A) (repeated cycle numbers)							Surviving (%)
		1	3	5	7	9	11	13	
1	**1** (524.5)	0.734	0.685	0.580	0.488	0.458	0.433	0.420	56.4
2	**1** + HOTEMPO	0.721	0.710	0.693	0.679	0.655	0.633	0.619	85.9
3	**5a** (531.5)	0.718	0.713	0.710	0.710	0.703	0.700	0.698	97.2
4	**1** + HOPEMP	0.723	0.709	0.698	0.683	0.671	0.657	0.646	89.3
5	**5b** (536.5)	0.709	0.699	0.592	0.680	0.669	0.659	0.649	91.5
6	**1** + HOTEMP	0.716	0.709	0.695	0.680	0.668	0.655	0.641	91.5
7	**5c** (538)	0.738	0.734	0.732	0.725	0.718	0.715	0.709	96.0
8	**1** + BPA	0.687	0.675	0.663	0.648	0.633	0.620	0.611	88.9
9	**5d** (547)	0.706	0.696	0.682	0.675	0.659	0.649	0.643	91.1
10	**1** + BHT	0.698	0.686	0.675	0.661	0.647	0.631	0.616	88.2
11	**5e** (537.5)	0.707	0.698	0.687	0.683	0.669	0.657	0.645	91.2
12	**2** (611)	0.864	0.860	0.852	0.845	0.837	0.830	0.810	93.4
13	**8a** (604.5)	0.804	0.803	0.799	0.800	0.797	0.793	0.787	96.9
14	**8b** (603.5)	0.718	0.713	0.710	0.710	0.703	0.700	0.698	97.9
15	**8c** (603)	0.792	0.791	0.790	0.789	0.786	0.787	0.784	99.0
16	**8d** (603)	0.739	0.737	0.735	0.734	0.732	0.727	0.725	98.1
17	**8e** (604)	0.758	0.757	0.752	0.751	0.750	0.747	0.745	98.0
18	**8f** (604.5)	0.726	0.724	0.721	0.720	0.718	0.715	0.710	97.8
19	**8g** (603.5)	0.709	0.707	0.705	0.701	0.698	0.693	0.690	97.3
20	**8h** (603)	0.711	0.710	0.705	0.702	0.699	0.695	0.689	96.9
21	**8i** (604)	0.712	0.710	0.705	0.700	0.695	0.690	0.685	96.2
22	**10** (606.5)	0.751	0.748	0.745	0.741	0.738	0.733	0.727	96.8

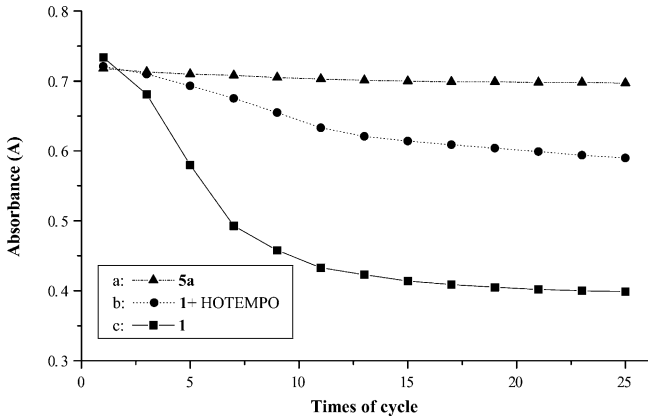


Fig. 3. The absorbance change of the photocolored state (merocyanine form) of: (a) compound **5a** ($\lambda_{max} = 536.5$ nm, $c = 5.0 \times 10^{-5}$ mol l^{-1}); (b) the mixture of compound **1** and HOTEMPO (1:1) ($\lambda_{max} = 524.5$ nm, $c = 5.0 \times 10^{-5}$ mol l^{-1}); (c) compound **1** ($\lambda_{max} = 524.5$ nm, $c = 5.0 \times 10^{-5}$ mol l^{-1}) in methanol solution in the repeated cycles of photocoloration and thermal decoloration.

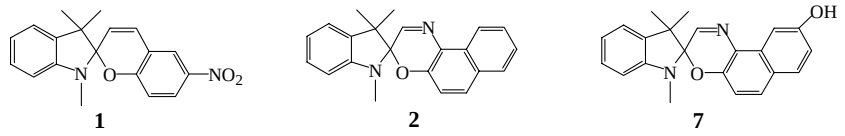
10^{-5} mol l^{-1}) were also prepared, respectively. The absorbance (A_0) of a solution at its λ_{max} was recorded immediately after irradiation with a 400 W high-pressure mercury lamp for 1 min, then the solution was irradiated with visible light to decolorize the solution by thermal process. The photocolorization and thermal decoloration cycle was repeated and the absorbance (A) at the λ_{max} in colored state was recorded. The results are listed in Table 5 and shown in Fig. 3.

3. Results and discussion

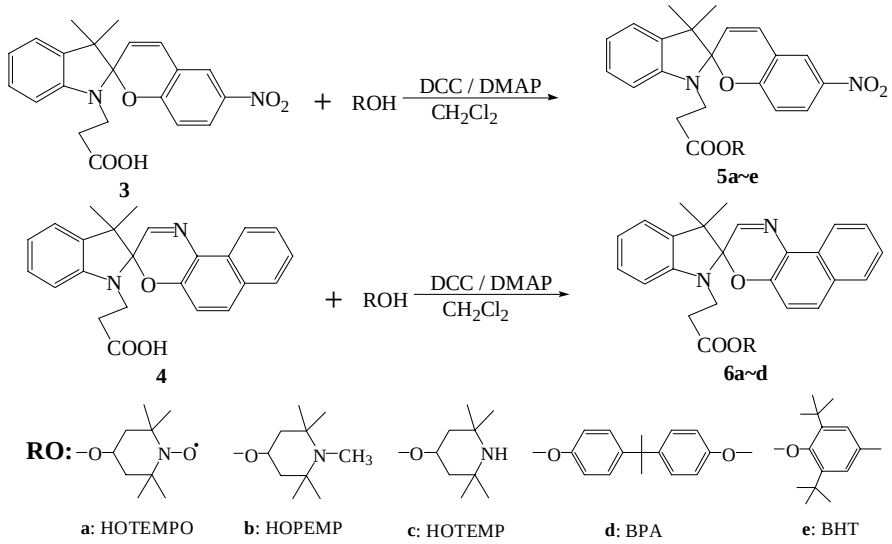
3.1. Synthesis of functionalized spiropyrans and spirooxazines

As reference spiro compounds for the newly synthesized spiropyrans and spirooxazines, compounds **1** [55] and **2** [50] (Scheme 2) were prepared according to the literatures.

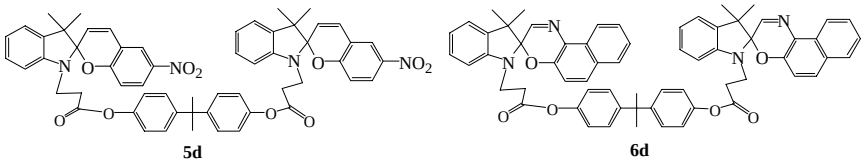
Antioxidants, 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy, 2,2,6,6-tetramethyl-4-piperidinol (HOTEMP), 1,2,2,6,6-pentamethyl-4-piperidinol (HOPEMP), bisphenol-A (BPA) and 2,6-di-*tert*-butyl-4-methyl-phenol (BHT) were selected as antioxidant pendants for the functionalization. For the synthesis of 1′,3′-dihydro-1′-substituted-3′,3′-dimethyl-6-nitro-spiro[2*H*-indole-2,2′-[3*H*]-benzopyran]s **5** and 1,3-dihydro-1-substituted-3,3-dimethyl-spiro[2*H*-indole-2,3′-[3*H*]-naphth-[2,1-*b*][1,4]-oxazine]s **6**, it was necessary to carry out the reaction under mild conditions with the consideration of the sensitive structures of the substrates. We selected a methodology of peptide syntheses using DCC for the condensation of spiropyran **3** and spirooxazine **4** having a propionic acid side chain at 1′-position with the antioxidants ROH (Schemes 3 and 4). Thus, new spiropyrans **5a**–**5e** and spirooxazines **6a**–**6d** were obtained in 39–71% yield, providing a convenient method for the synthesis of photochromic spiro compounds having a functional group.



Scheme 2. Reference spiro compounds.



Scheme 3. Synthesis of the spiro compounds having an antioxidant pendent.



Scheme 4. Structures of bis-spiropyran **5d** and bis-spirooxazine **6d**.

bis-Spironaphthooxazines **8a–8i** were synthesized with the modification of the Spivack and Pastor's procedure [35] by direct phosphorylation of spirooxazine **7** (Scheme 5). The phosphorylation proceeded smoothly with stirring a 2:1 molar mixture of compound **7** and a corresponding dichlorophosphate in toluene for 24 h at room temperature in the presence of DMAP as a promoter to afford phosphorylated bis-spirooxazines **8a–8i** in 70–91% yield. Similarly, bis-spirooxazine **10** was synthesized by a one-pot reaction (Scheme 5). Thus, compound **7** was firstly phosphinylated with dichlorophenylphosphine, and followed by the oxidation of phosphonite intermediate **9** at 45–50 °C using sulfur as the oxidant to give phosphonothionate **10** in 82% yield.

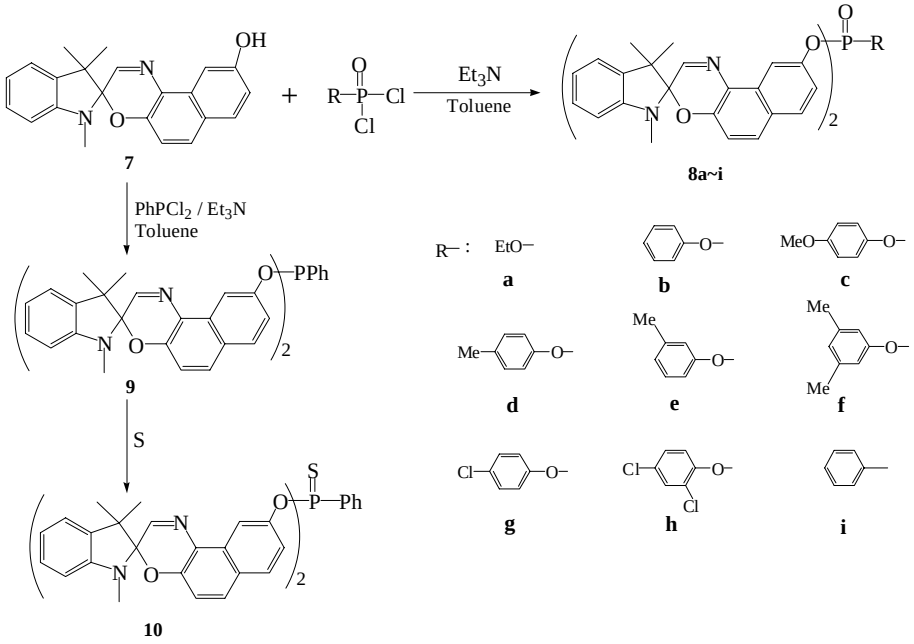
In addition, following the procedure of the synthesis of **5** and **6**, the symmetrical and unsymmetrical bis-spiro compounds **13–17** were prepared in 40–68% yield by the condensation of 1′-substituted carboxylic acid derivatives **3**, **4** and **12** with hydroxylated spiro compounds **7** and **11** (Scheme 6).

The structures of the newly synthesized compounds **5a–5e**, **6a–6d**, **8a–8i**, **10** and **13–17** were confirmed by ^{1}H NMR, ^{31}P NMR, IR, MS, UV and elemental analyses. As for compounds **5a** and **6a** their ^{1}H NMR spectra exhibited broad lines due to their paramagnetic nature which was shown by the presence of a typical nitroxide triplet signal in their ESR spectra.

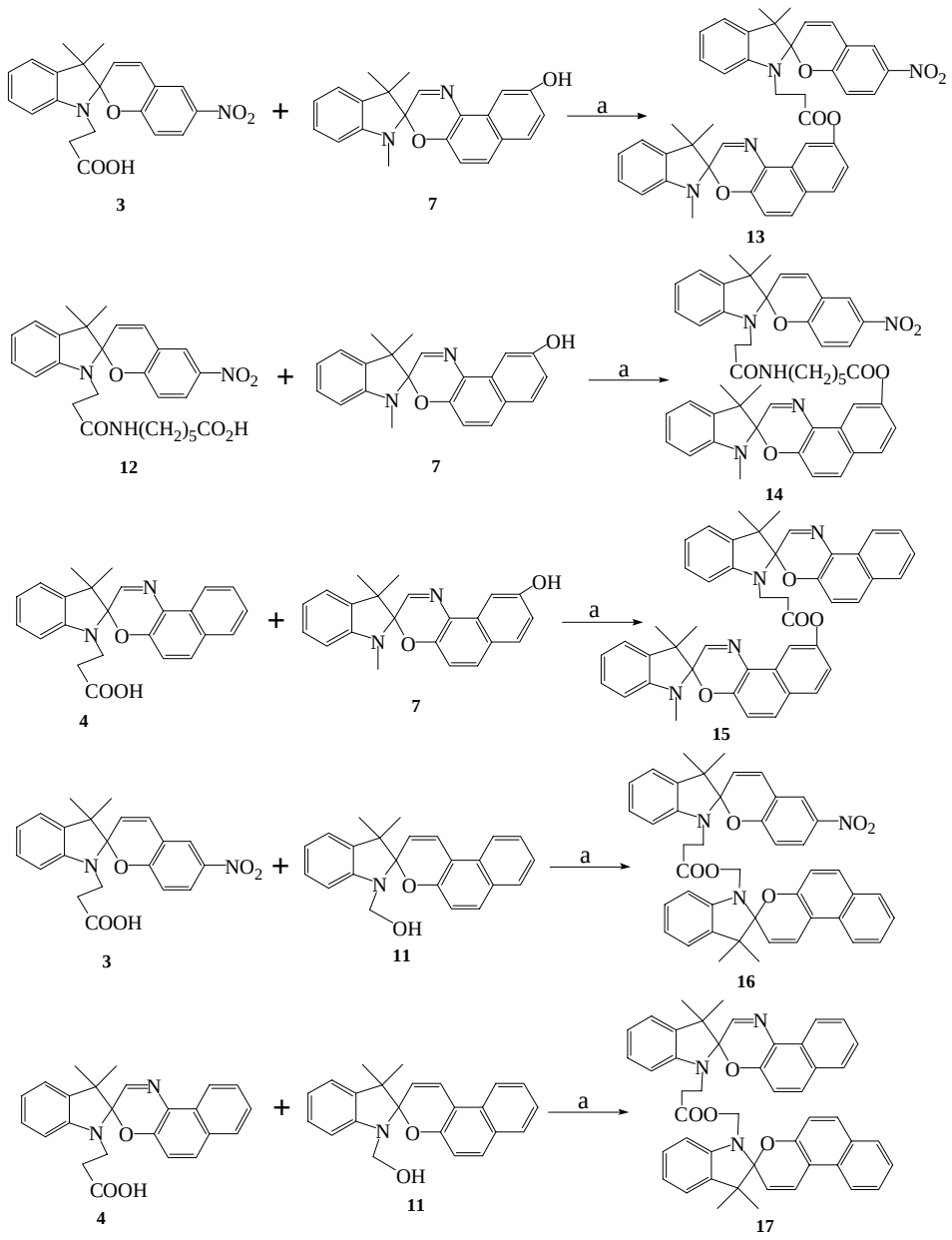
3.2. Photochromic properties

3.2.1. Absorption spectra of the closed spiro form

The absorption spectra of the functionalized spiro compounds **5a–5e**, **6a–6d**, **8a–8i**, **10** and **13–17** in various solvents were measured in the concentration of 1×10^{-5} to 1×10^{-4} mol l^{-1} and compared with those of the reference compounds **1**, **2** and **7**. They exhibited absorption maxima near 240, 270 and 340 nm in the closed form showing only small shifts of the maxima due to solvent polarity, similar to the parent reference compounds **1**, **2** and **7** (Table 1). The result indicates that neither intramolecular interaction between the spiro and the pendant antioxidant groups for **5a–5c**, **5e** and **6a–6c** nor between the two spiro groups for bis-spiro compounds **5d**, **6d**, **8a–8i**, **10** and **13–17** occurs in the ground state. The latter result coincides with the fact that the spectrum of a 1:1 mixture of spiropyran **1** and spirooxazine **2** was identical with the sum of those of **1** and **2**.



Scheme 5. Synthesis of bis-spironaphthooxazines.



Scheme 6. Synthesis of bis-spiro compounds. Reaction condition: (a) DCC/DMAP, CH_2Cl_2.

3.2.2. Absorption spectra of the colored merocyanine form

The absorption spectra of the colored open form of the spiro compounds **5a**–**5e**, **6a**–**6d**, **8a**–**8i**, **10** and **13**–**17** in various solvents were measured immediately after irradiation with a 400 W high-pressure mercury lamp for 30 s, and the λ_{max} are listed in Tables 2 and 3. As previously reported [33], the spiro photochromic compounds containing an antioxidant group **5a**–**5e** and **6a**–**6d** exhibited similar absorption spectra to those of their reference compounds **1** and **2**, respectively. In accordance with the previous observations [33], the visible absorption maxima of spiropyrans **5a**–**5e** underwent a hyperchromic shift in more polar solvents, while those of spirooxazines **6a**–**6d** did a hypsochromic shift. As shown in Table 2, the solvent effects on the chromatic shifts of spiropyrans **5a**–**5e** and spirooxazines **6a**–**6d** were less than on those of the corresponding reference compounds **1** and **2**, respectively, likely resulted from the interaction between the pendant group R and the photochromic part.

In addition, as shown in Table 3, similar photochromic behaviors were observed in the cases of the symmetric bis-spiropyrans **5e** and **16**, and the bis-spirooxazines **6d**, **8a**–**8i**, **10** and **15**. It should be noted that, compared with the reference compound **7**, compounds **8a**–**8i** and **10** having a phosphoryl short spacer linkage exhibited obviously weak solvent effect on the hypsochromic shift than compounds **6d** and **15** containing an esteric long spacer linkage, probably due to the more stronger intramolecular interaction

between the two photochromic parts and/or between the photochromic part and the phosphoryl group in **8a**–**8i** and **10**. As for the unsymmetric bis-spiro compounds **13** and **14**, the spiropyran part and the spirooxazine part exhibited their individual absorption spectral characters. In hexane solution the absorption maxima λ_{max} of both spiropyran part and spirooxazine part appeared around 580 nm, but in methanol the absorption maxima of spiropyran part ($\lambda_{max} \approx 559$ nm) and spirooxazine part ($\lambda_{max} \approx 602$ nm) were observed separately. The visible absorption spectra of the colored merocyanine forms of the unsymmetric bis-spiro compounds will be further discussed below (see Section 3.2.5).

3.2.3. The lifetime of the colored open form

The lifetimes of the colored merocyanine forms of bis-spironaphthooxazines **8a**–**8i** and **10** were found to be longer than that of the reference compounds **2** and **7**. This difference is exemplified by Fig. 1 which shows the decrease of the absorbances during the decoloration process at $\lambda_{max} = 578.5$ nm for **2**, at $\lambda_{max} = 579.5$ nm for compound **7** and at $\lambda_{max} = 589$ nm for compound **8b** after irradiation of solutions of compounds **2** (1.0×10^{-3} mol l^{-1}), **7** (1.0×10^{-3} mol l^{-1}) and **8b** (5.0×10^{-4} mol l^{-1}) in cyclohexane, respectively. The results indicated that the merocyanine group of compound **8b** might be stabilized by an intramolecular interaction between the two spiro photochromic groups, as reported in the case of the aggregate formation between two colored merocyanine forms or between colored merocyanine form and the colorless spiro form of spiropyrans in non-polar solvent [38,56]. It may also be reasonable to assume that the polar phosphoryl group stabilizes such aggregate formation.

3.2.4. The fatigue resistance of functionalized spiro photochromic compounds during the repeated photocoloration and thermal decoloration cycle

The kinetic analysis of the photodegradation process has been carried out in non-polar (cyclohexane) and polar (methanol) solvents. In both cases, spiropyrans **5a**–**5e** having an antioxidant pendant and bis-spironaphthooxazines compounds **8a**–**8i** and **10** connected through a phosphoryl group were found to exhibit higher fatigue resistance to continuous UV irradiation with a high-pressure mercury lamp in the air atmosphere than that of the reference compounds **1** and **2**, respectively. The rate of photodegradation was estimated by following the decrease of the absorbance at the λ_{max} of their colored merocyanine form.

As typical examples, Fig. 2a and b visualize that **5a** and **8b** undergo much slower photodegradation than their reference compounds **1** and **2**, respectively. For the series of spiro compounds **5a**–**5e**, **8a**–**8i** and **10**, their fatigue resistance were represented by a parameter $t_{A_0/2}$ which defines the time in minute required to decrease the initial absorbance (A_0) at the λ_{max} of their colored merocyanine form to the half value ($A_0/2$). The results, as shown in Table 4, indicated that the photodegradation of the spiro compounds were retarded remarkably by the introduction of antioxidant and phosphoryl groups. These groups played important roles in scavenging singlet oxygen or free radical species which have been considered to form during the photodegradation process [26].

The thermal decoloration of the colored merocyanine form of a spiro photochromic compound can be accelerated by a visible irradiation. Thus, the alternate irradiation with a mercury lamp and visible light gave a controlled photocoloration and thermal decoloration cycle. This method was utilized for evaluating the fatigue resistance ability of spiro photochromic compounds. Table 5 showed the decrease of the absorbance (A) at the λ_{max} of the merocyanine form of compound **1**, the mixture of compound **1** and an antioxidant (1:1), and the spiro photochromic compounds (**2**, **5**, **8** and **10**) in methanol solution in every repeated cycle. The fatigue resistance ability can be seen from the surviving (%) obtained after thirteen repeated cycles.

As shown in Table 5, the introduction of an antioxidant group as a pendant could remarkably enhance the fatigue resistance of the photochromic compounds. Interestingly, spiropyrans **5a**–**5e** linking an antioxidant pendant exhibited higher fatigue resistance than the 1:1 mixture of the parent reference compound **1** and the corresponding antioxidant. The result suggested that the antioxidant pendant group linked to the photochromic compounds could act synergetically as an inhibitor for photodegradation during the photocoloration and thermal decoloration cycles.

More detailed experiments were carried out, as shown in Fig. 3, with compound **1**, the mixture of compound **1** and HOTEMPO (1:1) and compound **5a** having an antioxidant group for 25 repeated cycles, respectively. It was found that the absorbances (A) of compound **5a** ($\lambda_{max} = 536.5$ nm; Fig. 3a) and the mixture of compound **1** and HOTEMPO (1:1, $\lambda_{max} = 529.5$ nm; Fig. 3b) in the merocyanine form showed a more slow decrease than in the case of compound **1** (Fig. 3c), especially in the first 10 cycles. It should be noted that after several cycles the solution of reference compound **1** could not decolorize completely after visible light irradiation, implying the decomposition of the merocyanine form or irreversible isomerization from the merocyanine form to the colorless spiro form.

These observations indicated that, in accordance with the data in Table 4, the functionalization with an antioxidant group or a phosphoryl group remarkably improved the fatigue resistance of the spiro photochromic compounds. In our previous report [33], we have shown that the introduction of a heteroaromatic pendant into spiropyrans and spirooxazines results in an inhibitory effect on their photostability. The present results provide a useful method for the improvement of the fatigue resistance of certain spiro photochromic compounds.

3.2.5. Intramolecular interaction involving the merocyanine group in bis-spiro compounds

Finally we paid attention to the intramolecular interaction involving the merocyanine groups of bis-spiro photochromic compounds in the photochromic process. It has been reported that the bis-spiro photochromic compound with a conjugated chain linkage exhibited an obviously different absorption spectrum, which reflected a remarkable change of the conjugation system in colored form compared with its parent compound [46]. For the bis-spiro photochromic compound connected through a non-conjugated chain, compared with its parent compounds, slightly different photochromic behaviors (such as λ_{max} and fatigue resistance) would be observed, when intramolecular interaction between the two merocyanine groups existed [47,48]. The discussion in Section 3.2.2 suggested the existence of the interaction between the two photochromic parts in the symmetric bis-spiro photochromic compounds **5d**, **6d**, **15**, **8a**–**8i**, **10** and **16**. Further information of the photochromic behaviors of the bis-spiro photochromic compounds would be obtained from the absorption spectra of the unsymmetric bis-spiro photochromic compounds **13** and **14**.

As shown in Table 3, in the unsymmetric bis-spiro photochromic compounds **13** and **14**, each of the spiropyran part and the spirooxazine part exhibited hyperchromic shift and hypsochromic shift individually, similar to the corresponding reference compounds **1** and **7**, respectively. In hexane solution, both of the spiropyran part and the spirooxazine part had similar absorption λ_{max} at around 580 nm. As the polarity of the solvent increased, the difference of the λ_{max} between the spiropyran part and the spirooxazine part enlarged because of the solvent effects. Consequently, broad absorption peaks at λ_{max} in the spectra of compounds **13** and **14** were observed as a result of the overlap of the absorption peaks of the spiropyran and the spirooxazine parts. In methanol, the difference of the λ_{max} between the spiropyran part and the spirooxazine part in compounds **13** and **14** was so big that two peaks contributed from the spiropyran and the spirooxazine parts appeared, implying that in compounds **13** and **14** both of the spiropyran part and the spirooxazine part kept their own merocyanine structural characteristics.

More detailed experiments were carried out with the methanol solution of the unsymmetric bis-spiro photochromic compounds **13** and **14**, and the reference compounds **1** and **7**. Fig. 4 showed the absorption spectra of reference compounds **1** (a) and **7** (b), the mixture of compounds **1** and **7** (c), and the unsymmetric bis-spiro compound **13** (d) in methanol solution before and after UV irradiation. The absorption spectral curve (marked with asterisk) of the mixture of compounds **1** and **7** in visible region was virtually superimposable with the summation spectral curve of compounds **1** and **7**, indicating that there is no intermolecular interaction between the merocyanine forms of compounds **1** and **7** in the methanol solution at 10^{-4} mol l^{-1} concentration. In contrast, the spectral curve

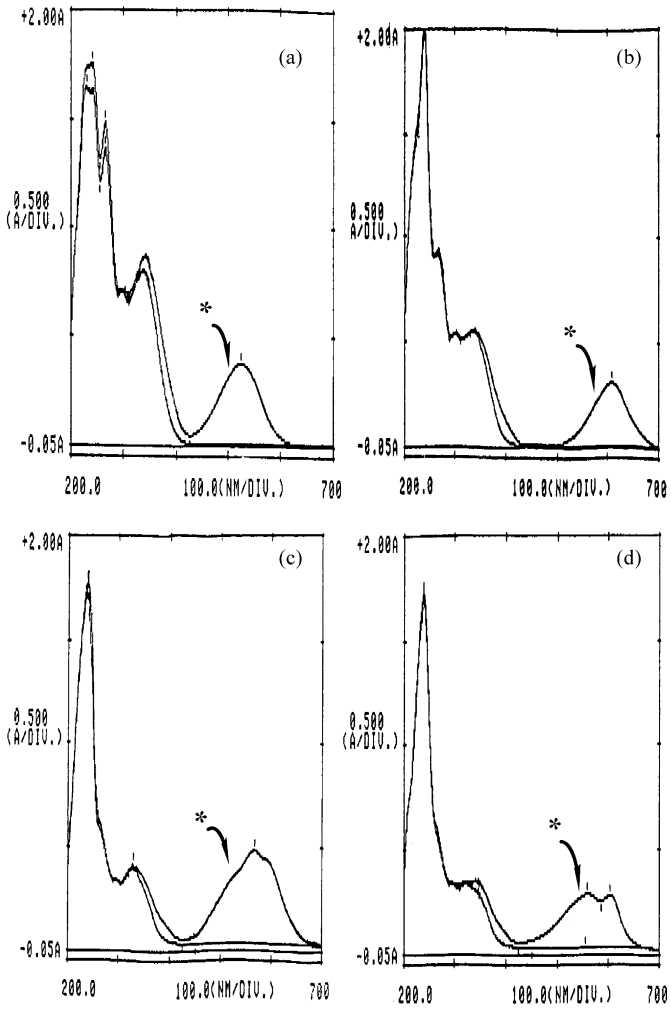


Fig. 4. The absorption spectra of: (a) compound **1**; (b) compound **7**; (c) the mixture of compounds **1** and **7** (1:1); and (d) compound **13** in methanol solution ($c = 1.0 \times 10^{-4}$ mol l^{-1}) before and after (curve marked with asterisk) UV irradiation for 30 s.

of **13** (Fig. 4d) was not superimposable with the summation spectral curve of compounds **1** and **7**, implying that there exists an intramolecular interaction between the merocyanine groups of compound **13**. A similar result was observed for the absorption spectrum of compound **14**.

In conclusion, we have synthesized series of spiropyrans and spirooxazines containing an antioxidant group, and bis-spiro photochromic compounds connected through a non-conjugated esteric or phosphoryl chain using a convenient method, and investigated the photochromic behaviors of the newly synthesized compounds with the comparison of the reference compounds. The introduction of an antioxidant or a phosphoryl group remarkably improved the fatigue resistance and the stability of the merocyanine form of the spiro photochromic compounds. The bis-spiro photochromic compounds existed an intramolecular interaction between the two merocyanine groups in solution.

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