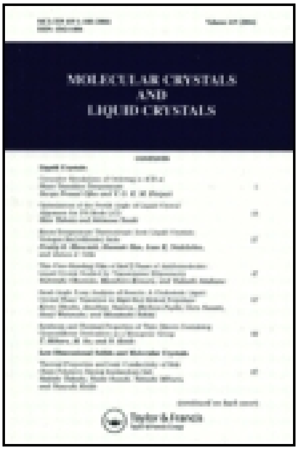

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Synthesis and Photochromic Behaviors of Spiropyrans and Spirooxazines Containing an Antioxidant Group

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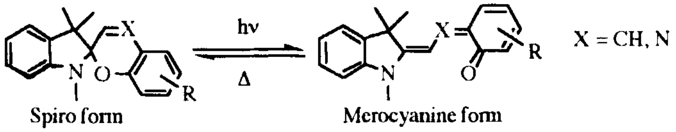
Two series of novel spiropyrans and spirooxazines containing an antioxidant group as a pendant were synthesized by a convenient method. Their photochromic behaviors and photostabilty were investigated with the aid of absorption spectral measurements, showing that they exhibited higher fatigue resistance than that of the parent spiro-compounds.

Keywords: spiropyrans; spirooxazines; antioxidants; photochromism; fatigue resistance

INTRODUCTION

The chemistry of photochromic spiro-compounds has been studied extensively.[1,2] with regard to industrial applications as photoresponsive materials.[3-6] One of the major limiting factors for the applications is the photodegradation process (fatigue phenomenon) occurring during the reversible coloration-decoloration cycle of the following scheme resulting from repeated exposure to UV radiation.[2]



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The photostability of photochromic spiro-compounds has been widely investigated in terms of the degradation mechanism in solution and in polymer matrix.[7] Recently, Guglielmetti et al.[8] proposed a number of mechanisms for the oxidative degradation processes, which occurred by free radical or singlet oxygen formation. A considerable increase of the fatigue resistance has been observed by adding 1,4-diazabicyclo[2.2.2]octane, a singlet oxygen quencher.[9]

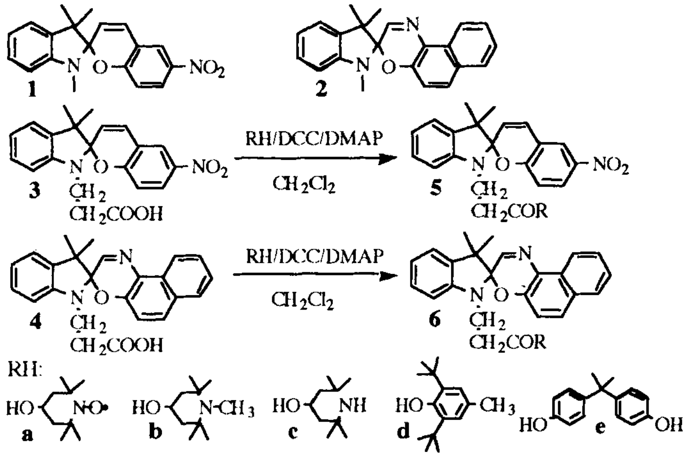
In order to improve the fatigue resistance of photochromic compounds, we investigated on the synthesis of a series of novel spiropyrans and spirooxazines containing an antioxidant group, such as 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (HOTEMPO), 2,2,6,6-tetramethyl-4-piperidinol (HOTEMP), 1,2,2,6,6-pentamethyl-4-piperidinol (HOPEMP), 2,6-di(tert-butyl)-4-methylphenol (BHT) and bisphenol-A (BPA) and on their photochromic behaviors.

RESULTS AND DISCUSSION

Synthesis

The reference compounds **1** [10] and **2** [11] were synthesized according to the literatures. For the synthesis of 1',3'-dihydro-1'-substituted-3,3'-dimethyl-6-nitro-spiro[2H-indole-2,3'-[3H]benzo-pyran]s (**5**) and 1,3-dihydro-1-substituted-3,3-dimethylspiro[2H-indole2,3'[3H]naphth-[2,1b][1,4]-oxazine]s (**6**) , we chose a methodology[12] of peptide syntheses using dicyclohexylcarbodiimide (DCC) and 4-dimethylamino-pyridine (DMAP) for the condensation of a spiropyran **3** and a spirooxazine **4** having a propionic acid side chain with various antioxidant compounds (RH). Thus, **5a–5e**, **6a–6c** and **6e** were obtained in the yields of 39~71%, providing a convenient method for synthesizing photochromic spiro-compounds containing a complex functional group.

The structures of compounds **5** and **6** were confirmed by ^{1}HNMR, IR, MS, UV, and elemental analyses. For compounds **5a** and **6a**, their ^{1}HNMR spectra exhibited broad lines due to their paramagnetic nature



which was confirmed by the presence of a typical nitroxide triplet signal in their ESR spectra.

Photochromism

The photochromic behaviors of compounds **5** and **6** in selected solvents were investigated with the aid of UV spectral measurements. Compounds **5** and **6** exhibited UV absorption maxima near 240, 270 and 340 nm in the closed form, similar to the reference compounds **1** and **2** showing no shift due to solvent polarity . The λmax of **5** and **6** for the colored open form in cyclohexane and methanol shown in Table 1 were taken in $1.0 \times 10^{-5} \sim 1.0 \times 10^{-4}$ mol L^{-1} solutions after irradiating for 30 seconds with a high-pressure mercury lamp. Compounds **5** and **6**, have λmax at wavelengths similar to those of their reference compounds **1** and **2**, respectively, indicating no spatial interaction between the functional group R and the photochromic part. In accordance with the previous observations,[13] the visible absorption maxima of spiropyrans **5a~5e** showed a hypsochromic shift in more polar solvents, while those of spirooxazine **6a~6d** did a hyperchromic shift.

In cyclohexane solution, the colored open forms of compounds **5** exhibited higher photostability to continuous irradiation than that of the reference compound **1**. The photostability could be described by a parameter $t_{A_0/2}$ (time in minutes necessary to reduce the initial colorability A_0 to $A_0/2$) which represents fatigue resistance. Under a continuous irradiation with a high-pressure mercury lamp in the air atmosphere, the absorbance at λmax of each compound reached rapidly up to the maximum value (A_0), then the value decreased gradually due to the photodegradation. The decrease of absorbance of compounds **5** was much slower than that of the parent reference compound **1**, which could be also seen from $t_{A_0/2}$ shown in Table 1. The results indicated that the fatigue resistance of compounds **5** was improved remarkably due to the introduction of the antioxidant group. The antioxidant groups of photochromic compounds **5** could quench singlet oxygen or scavenge free radical species formed in the photodegradation process,[8,9] enhancing the fatigue resistance of the compounds.

The thermal decoloration of the colored open form of the spiro-compounds **5** and **6** can be accelerated by irradiation with an infrared lamp. Thus the alternate irradiation with the mercury and infrared lamps gave a photocoloration-thermal decoloration cycle. Figure 1 showed the relationship between absorbances at λmax (524.5nm) of photocolored state (A) and thermally decolored state (B) of compounds **1** (a) and **5a** (b). It was found that the absorbance at λmax of the photocoloration state decreased with the increase of the repeated cycle numbers. In contrast, the absorbance of the decolored state at 524.5 nm increased during the process. The decrease of absorbance in colored state was attributable to the photodegradation of the photochromic material, and the increase of the absorbance in the decolored state was likely due to the accumulation of the photodegradation products.[9] Figure 1(b) showed that **5a** having HOTEMPO have higher fatigue resistance than that of reference compound **1**.

More detailed experiments were carried out with methanol solutions of the reference compound **1**, the mixture of compound **1** and an antioxidant, and compounds **5** having an antioxidant pendant. Table 2 listed changes of the absorbance at lmax of each sample solution with thirteen repeated cycles of the photocoloration-thermal decoloration process. It was found that the addition of an antioxidant could

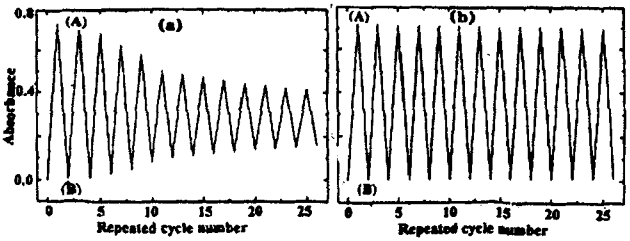
Table 1. The λmax of the merocyanine form of spiro-compounds **1**, **5**, **2** and **6** and the time $t_{Ao/2}$ (min) necessary to reduce the initial colorability Ao to Ao/2 for spiropyrans **1** and **5** in cyclohexane.

λmax,nm	**1**	**5a**	**5b**	**5c**	**5d**	**5e**	**2**	**6a**	**6b**	**6c**	**6e**
C_6H_{12}	580.5 612	602	581.5	586	583.5	588.5	578.5	567	577	580	580
MεOH	524.5	536.5	538	537.5	533.5	547	611	619	607.5	605	605
$t_{A_0}/2$	12	690	570	540	360	300 min	—	—	—	—	—

Table 2. The changes of absorbance at the λmax of **1**, a 1 : 1 mixture of **1** and an antioxidant, and **5** in methanol at every repeated cycle of the photocoloration and thermal decolorization.

Compounds	Repeated cycle numbers							Decreasing
(λmax,nm)	1	3	5	7	9	11	13	%
1 (524.5)	0.734	0.685	0.580	0.488	0.458	0.433	0.420	56.4
1 + HOTEMPO	0.721	0.710	0.693	0.679	0.655	0.633	0.619	85.9
5a (536.5)	0.718	0.713	0.710	0.710	0.703	0.700	0.698	97.2
1 + HOPEMP	0.723	0.709	0.698.	0.683	0.671	0.657	0.646	89.3
5b (538)	0.709	0.699	0.692	0.680	0.669	0.659	0.649	91.5
1 + HOTEMP	0.716	0.709	0.695	0.680	0.668	0.655	0.641	89.5
5c (537.5)	0.738	0.734	0.732	0.725	0.718	0.715	0.709	96.0
1 + BHT	0.698	0.686	0.675	0.661	0.647	0.631	0.616	88.2
5d (533.5)	0.707	0.698	0.687	0.683	0.669	0.657	0.645	91.2
1 + BPA	0.687	0.675	0.663	0.648	0.633	0.620	0.611	88.9
5e (547)	0.706	0.696	0.682	0.675	0.659	0.649	0.643	91.1

Figure 1. Absorbance changes at the λmax of the photocolored state (A) and the decolored state (B) at every repeated cycle. (a) **1**; (b) **5a**.



remarkably enhance the fatigue resistance of the photochromic compounds. Interestingly, compounds **5a**~**5e** having an antioxidant pendant exhibited higher photostability than the mixture of the reference compound **1** and an antioxidant. In our previous report,[13] we have shown that the introduction of a heteroaromatic pendant into spiropyrans and spirooxazines results in an inhibitory effect on their photostability. The results suggested that the antioxidant pendant group could act synergetically as an inhibitor for photodegradation during the photocoloration-thermal decoloration cycle.

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