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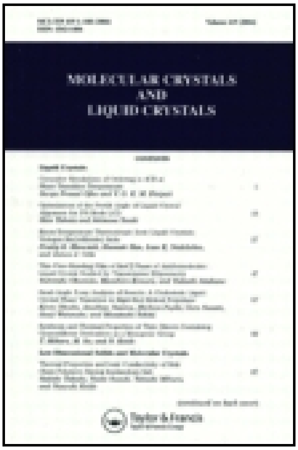

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Synthesis and Photochromic Behaviors of Novel Bis-spiro-naphthooxazines Connected Through a Phosphoryl Group

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Synthesis and Photochromic Behaviors of Novel Bis-spiro-naphthooxazines Connected Through a Phosphoryl Group

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A series of novel bis-spironaphthooxazines (**3a**~**3i**) and (**4**) containing a phosphoryl group were synthesized in 70~91% yield. Their photochromic behaviors and photostabilty were investigated with the aid of absorption spectral measurements, showing that they exhibited higher fatigue resistance in the coloration and decoloration cycle than that of the parent reference compound **1**.

Keywords: bis-spironaphthooxazines; photochromism; fatigue resistance

INTRODUCTION

Spironaphthooxazines are one of the well-known photochromic compounds which are typically exploited for many applications of relevant industrial impact.[1-3] They undergo a reversible opening of the oxazine ring induced by UV light producing the colored merocyanine form and ring closure induced thermally as in scheme below.[4]

However, irreversible color change called fatigue phenomenon inevitably occurs during repeated coloration-decoloration cycle due to the irreversible photodegradation of the photochromic species after a long exposure to UV irradiation.[5] This fatigue phenomenon is one major problem with photochromic compounds limiting their industrial

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applications.[4] The photodegradation occurs via the formation of radical intermediates or singlet oxygen. Some approaches to improve their photostability have recently made by adding or chemically binding a singlet oxygen quencher,[6] antioxidant[7,8] and spin-trapping agent[9] to the photochromic systems. We have shown that the introduction of an antioxidant moiety into spiropyrans and spirooxazines exhibits an increase of the fatigue resistance.[7]

Here we descibe an attempt to improve the fatigue resistance of spirooxazines by the introduction of a phosphoryl group into them. Aryl or alkyl phosphate compounds have been used as antioxidant and photostabilizer in many fields.[10] A photochromic liquid compostion containing phosphine derivatives hasdecresed the degradation rate.[11]

RESULTS AND DISCUSSION

Synthesis

Aryl and alkyl dichlorophosphates ($RPOCl_2$),[12] the reference compound **1** and the starting compound **2** were synthesized according to the literature.[13] Bis-spironaphthooxazines **3a–3i** were synthesized with a modification of the Spivack's procedure[10] by direct phosphorylation of spirooxazine **2**. The phosphorylation proceeded smoothly with stirring a 2 : 1 molar mixture of **2** and a dichlorophosphate in toluene for 24 hours at room temperature in the presence of DMAP (4-dimethylaminopyridine) as a promoter to afford phosphorylated bis-spirooxazines **3a–3i** in 70–91% yield. Compound **4** was synthesized in an one-pot reaction. Thus compound **2** was phosphinylated by dichlorophenylphosphine. The reaction was followed by the oxidation of a phosphonite intermediate at 45–50°C using sulfur as the oxidant to give phosphonothionate **4**. The structures of **3a–3i** and **4** were confirmed by ^{1}HNMR, ^{31}PNMR, IR, MS, UV, and elemental analyses.

Photochromism

The photochromic behaviors of compounds **3a~3i** and **4** in various solvents were examined with the aid of absorption spectroscopy in comparison to those of the reference compound **1**.

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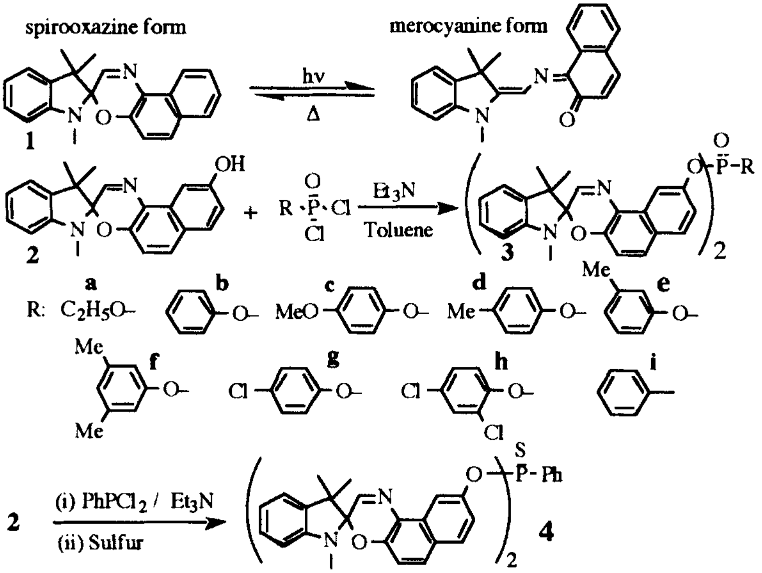

Absorption spectra of the closed spirooxazine form. Spirooxazines **3a~3i** and **4** in the ring-closed form exhibited absorption maxima near 240, 270 and 340 nm similar to those of the reference compound **1**, showing only small shifts of the maxima due to solvent polarity in accordance with those of spirooxazines derivatives previously reported.[7,8] The result indicates that no intramolecular interaction among the phosphoryl and two spirooxazine groups nor occours in the ground state.

Absorption spectra of the colored open form. The λmax of **3a–3i** and **4** in the colored merocyanine form in cyclohexane and methanol were taken at 5.0×10^{-4}–1.0×10^{-3} mol L^{-1} concentrations in around 20 seconds after irradiation the solutions for 30 seconds with a 400W high-pressure mercury lamp (Pyrex housing) and compared with that of the reference compound **1**. A strong absorption band at the visible region (585–606.5 nm) depends upon the solvent polarity for **3a–3i** and **4**, showing hyperchromic shifts in more polar solvents. The absorption maximum of **1** appears at a wider region (578.5–611 nm) than those of **3** and **4** showing similar solvent shifts.

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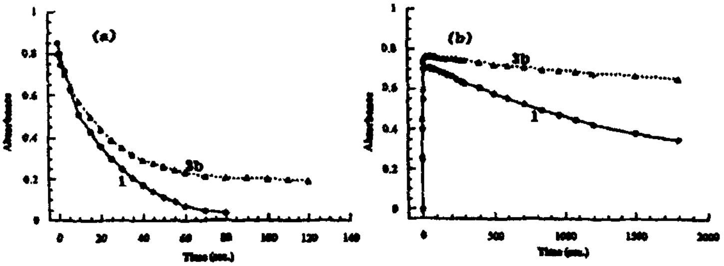
Table 1. The λmax (nm) of the merocyanine form of **1**, **3a–3i** and **4** and the time $t_{Ao/2}$ (min.) necessary to reduce the initial colorability Ao to Ao/2 for **1**, **3a–3i** and **4** in cyclohexane.

λmax,nm	**1**	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**	**3h**	**3i**	**4**
C_6H_{12}	578.5	589	589.5	586.5	588.5	587.5	589	588	587	586.5	585.5
MeOH	611	604.5	603.5	603	603	604	604.5	603.5	603	604	606.5
$t_{Ao/2}$	50 min	150	170	180	165	175	160	155	150	135	120

Table 2. The changes of absorbance at the λmax of **1**, **3a–3i** and **4** in methanol in the repeated photocoloration–thermal decolorization cycle.

Compounds	Repeated cycle numbers							Surviving
(λmax,nm)	1	3	5	7	9	11	13	%
1 (524.5)	0.864	0.860	0.852	0.845	0.837	0.830	0.810	93.4
3a (604.5)	0.804	0.803	0.799	0.800	0.797	0.793	0.787	96.9
3b (603.5)	0.718	0.713	0.710	0.710	0.703	0.700	0.698	97.9
3c (603)	0.792	0.791	0.790.	0.789	0.786	0.787	0.784	99.0
3d (603)	0.739	0.737	0.735	0.734	0.732	0.727	0.725	98.1
3e (604)	0.758	0.757	0.752	0.751	0.750	0.747	0.745	98.0
3f (604.5)	0.726	0.724	0.721	0.720	0.718	0.715	0.710	97.8
3g (603.5)	0.709	0.707	0.705	0.701	0.698	0.693	0.690	97.3
3h (603)	0.711	0.710	0.705	0.702	0.699	0.695	0.689	96.9
3i (604)	0.712	0.710	0.705	0.700	0.695	0.690	0.685	96.2
4 (606.5)	0.751	0.748	0.745	0.741	0.738	0.733	0.727	96.8

Figure 1. The changes of absorbance at the λmax of **1** (578.5 nm; 1 x 10^{-3} mol L^{-1}) and **3b** (589.5 nm; 5.0 x 10^{-4} mol L^{-1}) in cyclohexane at room temperature: (a) representing the lifetime of the merocyanine form in the decoloration process and (b) representing the photodegradation rate of the substrate under continuous UV-irradiation.



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The lifetime of the colored open form (merocyanine form) in the thermal decoloration process. The lifetimes of the colored open forms of **3** and **4** were found to be longer than that of **1**. This difference is exemplified by Figure 1 (a) which shows the decrease of the absorbances at 578.5 nm for **1** and at 589 nm for **3b** after irradiation of solutions of **1** and **3b** in cyclohexane. The results suggest that the polar phosphorryl group may stabilize the merocyanine form of compound **3** due to its interaction with the colored merocyanine form, as reported in the case of the aggregate formation between two colored merocyanine forms or between the colored merocyanine form and the colorless spiro form of spiropyrans in nonpolar solvents.[14,15]

The photodegradation (fatigue phenomenon) of spirooxazines during the photochromic cycle. The photostability of **3a–3i** and **4** was estimated by two different methods in comparison with that of **1**. The photostability can be described by a parameter $t_{Ao/2}$.[8] This parameter, which represents fatigue resistance, shows time (in minutes) necessary to reduce the initial colorability Ao to Ao/2. Under continuous irradiation conditions (high-pressure mercury lamp with Pyrex housing) in the air atmosphere, the absorbance of the λmax of each compound reached rapidly up to the maximum value (Ao), then the absorbance decreased gradually due to the photodegradation of the compounds as illustrated in Figure 1(b) for compounds **1** and **3b**. The decrease of absorbance of compounds **3** was much slower than that of the reference compound 1. This was also seen from Table 1 which showed the $t_{Ao/2}$ values contained for compounds **1**, **3a–3i** and **4**.

The thermal decoloration of the colored open form of the spirooxazines **3** 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.[8] Table 2 listed the changes of the absorbance at λmax of thereference compound **1** and compounds **3a–3i** and **4** in methanolic solution with thirteen repeated cycles of the photocoloration-thermal decoloration process. It was found that compounds **3** and **4** exhibited higher photostability than the

reference compound 1, suggesting that the introduction of phosphoryl group could considerably improve the fatigue resistance of spirooxazines.

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