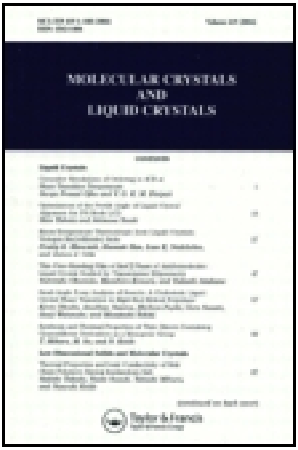

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Structure Effect on Photochromic Mechanism of Spirooxazines

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Structure effect on photochromic mechanism of 1,3,3-trimethylspiro[indoline-2,3′-[3H]naphtho[2,1,-b][1,4]oxazine] (SP1), 1,3-Dimethyl-3,2′-(1,3 -propylene)spiro[indoline-2,3′-[3H] naphtho[2,1-b][1,4]oxazine] (SP2) and 1,2′-(1,3-propylene),3,3-dimethylspiro[indo- line-2,3′ [3H]naphtho[2,1-b][1,4]oxazine](SP3) have been studied by nanosecond laser photolysis. Because of different connective positions of 1,3-propylene group in SP2 and SP3, the photochromic behaviours of them are quite different. One photoproduct of SP2 was only detected, and its lifetime is about 0.15μs. However, two colored forms of SP3 were detected after UV irradiation. The lifetimes of them are much longer than that of C-SP2. The semiempirical computational results by AM1 method were coincided with the experimental results.

Keywords: Photochromism; Spirooxazines; Structure effect; Laser photolysis; AM1 calculation

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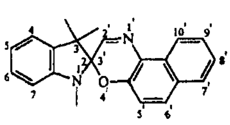
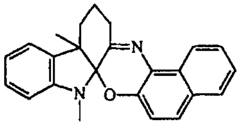
INTRODUCTION

Photochromic spirooxazine was reviewed recently [1]. The substitutuents effects on indoline and naphtho moieties of SP1 have been studied very well. Several papers were published with respect to photochromic mechanism of spirooxazines[2-7]. However the substituent effect on oxazine moiety was studied rarely [5-7], because there is only one position, 2'-position, in oxazine ring can be substituted.

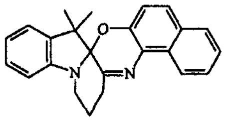
This paper will be emphasized on the photochromic intermediate, final products and reaction mechanism of 1,2' and 3,2' positions linked three ring system photochromic compounds, SP2 and SP3. The structures are shown as following



SP1



SP2



SP3

EXPERIMENTAL

Materials

SP1 was purchased from Aldrich, SP2 was synthesized according to literature method [6].

SP3 was synthesized as follow. To a mixture of 1,2-(butylene-1,4)-3,3-dimethylindolenium iodide (1.00 g, 3.06 mmol), ether (20ml), and water (10 ml) in 100 ml flask was added solid sodium hydroxide(0.37 g, 9.18 mmol, 3.0 eq) and the mixture was stirred for 1.5hrs at room temperature. The organic layer was separated, washed with water, dried with sodium sulfate, and then concentrated in vacuo. After the residue was dissolved in 10 ml ethanol in a 50 ml flask, 1-nitroso-2-naphthol (0.53 g,3.06 mmol) was added and the mixture was refluxed for 2.5 h. After the solvent was removed in vacuo, the residue was chromatographed to give 223 mg (0.63 mmol, 21%, m.p. 157℃) of SP3.

Cycloxehane (CHX) and acetonitrile (ACN) are spectral reagent, and used without further purify.

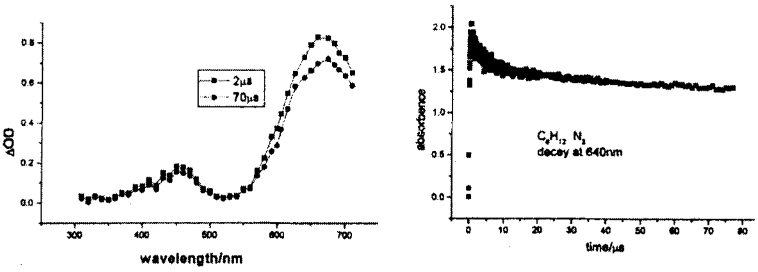
An eximer laser was used as excitation source[8].

RESULT AND DISCUSSION

Absorption spectra and Decay kenitics of transient species of spirooxazines

The transient absorption spectra and decay kenitics of SP1 and SP2 have been studied [2-7]. The steady state photochromism of SP3 had also been studies [9]. SP3 was irradiated with 366nm Light at -5℃ in chloroform to form a colored form (C1-SP3) which has an absorption peak at 650nm. When C1-SP3 was irradiated with 608nm light, it was changed to a second colored form (C2-SP3) with an absorption maximun wavelength at 545nm. The later species was not changed photochemically or thermally at room temperature.

When a solution of SP3 in CHX and ACN was irradiated with an excimer laser to form colored forms The transient absorption spectra in ACN and decay curve in CHX were shown in Figure 1(a) and Figure 1(b). The absorption maximum wavelength are 640nm in CHX and 670 nm in ACN respectively. The decay obeyed obviously two exponential decay as shown in Figure 1(b). The fast decay and slow decay species were analysed with two first order kenitic method. The results were summarized in table 1.



(a) (b)

Figure 1 (a) Transient absorption spectrum of SP3 in ACN(N_2 bubbling). (b)Decay curve of the colored forms of SP3 in CHX(monitored at 640nm)

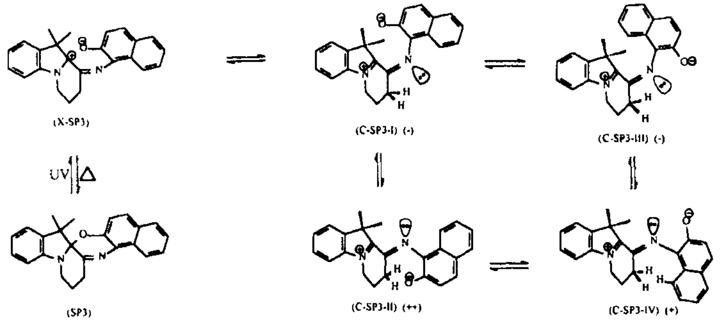
Table 1 Decay constants (k) and halflife($t_{1/2}$) of photoproducts(C-SP3s)

Solvent	Photoproducts			
	C-SP3-IV		C-SP3-II	
	$k_1 \times 10^{-3}(s^{-1})$	$t_{1/2}(\mu s)$	$k_2 \times 10^{-3}(s^{-1})$	$t_{1/2}(\mu s)$
CHX	23.70	29.2	2.61	262
ACN	3.08	225	1.50	462

The decay constant of fast decay species was larger than slow decay one with almost one order magnitude in CHX. However, the difference of decay constants, between two species was only about twice in ACN.

According to the literature [2-4], after laser pulse irradiation of SP1, the bond cleavage of spiro-carbon and oxygen occur within 3ps to form an intermediate (X) and then to form colored forms (C-SP1s). within 20ps.

The formation of C-SP3s is much slower than that of C-SP1s, and obeyed first order kinetical rule.The rate constants of formation of C-SP3 were $3.33\times10^{7}s^{-1}$ in acetonitrile. The photochromism of SP3 is shown in Scheme 1

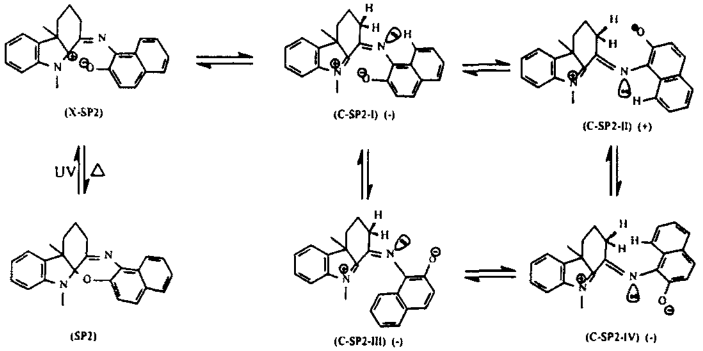


Scheme1: Photochromism of SP3 and Thermal conversion of C-SP3s (plus (+) indicates the molecule is relative stable; negative (-) indicates the molecule is relative unstable)

The first step of photochromism for SP3 is spiro-C-O bond cleavage at the first excited singlet state to form an intermediate (X-SP3), as the same as SP1. X-SP3 was transferred into C-SP3-I via molecular charge reorganization and intramolecular hydrogen bond formation between lone electron pair of nitrogen and hydrogen. C-SP3-I may have two paths further to transfer to C-SP3-II, via C=N double bond reversion, another way is N-C single bond rotation to form C-SP3-III. Because of stereohindrance of naphthyl ring with two methyl groups and negative charge repulsion between oxygen anion and lone electron pair of nitrogen, C-SP3-III is relative unstable, and could further transfer to C-SP3-IV or back to C-SP3-I. An equilibrium between C-SP3-II and C-SP3-IV could also exist. Because of the charge repulsion and stereohindrance in C-SP3-IV, the equilibrium is obvious favourable to C-SP3-II.

Based on above description, two substable colored forms, C-SP3-II and C-SP3-IV could be detected, the long life time species could be assigned to C-SP3-II and the shorter one should be C-SP3-IV. The bonds reorganization from X-SP3 to C-SP3s is slower than that of SP1 because of sterohindrance of 1,3-propylene and two methyl groups. This is possible reason that we can determine the formation cruve after laser pulse.

Fan et al [6] reported that one lifetime of colored form of SP2 was detected which is 0.15 μ s, and much shorter than C-SP3s. The photochromism and thermal conversion were shown in scheme 2.



Scheme 2: Photochromism of SP2 and Thermal conversion of C-SP2s (plus (+) indicates the molecule is relative stable; negative (-) indicates the molecule is relative unstable)

In the case of SP2, the detectable species may be C-SP2-II. C-SP2-II could be formed from C-SP2-I via N=C double bond reversion. If C-SP2-I were transferred to C-SP2-III, it should be overcome the interaction between the positive and negative charge. It is obvious that the equilibrium is much unfavourable to form C-SP2-III. C-SP2-IV could be formed from C-SP2-II or C-SP2-III, because of sterohindrance of naphthyl ring with cyclohexanyl ring and negative charge repulsion between oxygen anion and lone electron pair of nitrogen. It could be very unstable.

Semiempirical computational result

Semiempirical AM1[10] method was used to optimize the photoproducts. The formation heat of colored forms was calculated by the AM1 computational method (table 1). It is indicated that C-SP2-II could be the most stable colored form of SP2, however there are two colored forms which could be detected for SP3.

Table 1, The formation heat of the colored forms of SP2 (KJ)

C-SP2-I	C-SP2-II	C-SP2-III	C-SP2-IV
416.27103	368.59707	379.57480	373.57157

C-SP3-I	C-SP3-II	C-SP3-III	C-SP3-IV
547.98766	361.42630	451.61677	369.92344

Based on the results of AM1 calculation, it was also found that the formation of intramolecular hydrogen bonds is the one of main reasons for their stability.

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