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Fluorescence and photoinversion reactions in solutions of chiral diaryl sulfoxides with various sizes of aromatic rings

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Abstract

Chiral aryl 4-tolyl sulfoxides substituted with several sizes of aromatic rings, (S)-(−)-phenyl 4-tolyl sulfoxide (PHSO), (R)-(+)-1-naphthyl 4-tolyl sulfoxide (NASO), (R)-(+)-9-phenanthryl 4-tolyl sulfoxide (PNSO), and (R)-(+)-1-pyrenyl 4-tolyl sulfoxide (PYSO), were prepared. It has turned out for the first time that there are n–σ^*, π–σ^* and π–π^* states in excited states of these molecules by MO calculation. Fluorescence spectra and quantum yields of fluorescence, Φ_{fl}, were measured in polar and non-polar solvents. Quantum yields of photoinversion, Φ_{inv}, and photolysis, Φ_{dec}, were also obtained with CD and HPLC measurements. Aromatic-ketone like characteristics have been noticed in the fluorescence measurements, i.e., fluorescence has been observed from sulfoxides substituted with large aromatic rings and their fluorescence becomes strong in a polar solvent. We attributed these characteristics to the decrease in π–π^* transition energy as the degree of conjugation increases, while n–σ^* and π–σ^* transition energy does not decrease so much. The values of Φ_{inv} and Φ_{dec} for PHSO, NASO and PNSO were found to be 0.3–0.4 (Φ_{inv}) and 0.03–0.05 (Φ_{dec}). The quantum yields for PYSO were measured as $\Phi_{\mathrm{inv}} = 0.02$–$0.03$ in methanol and hexane, and $\Phi_{\mathrm{dec}} = 0.002$–$0.003$ in methanol and 0.012–0.016 in hexane. It was found that quantum yields of photoinversion and photolysis decrease as the π–π^* transition energy decreases. We concluded that photoinversion occur during change in electronic states from n–σ^* states to the ground state.

Keywords: Fluorescence; Photoinversion; Photoracemization; Photolysis; Chiral; Sulfoxide

1. Introduction

Chirality is an important feature of organic molecules. Investigations of asymmetric organic reactions in ground states have shown dramatic development, and the importance of studies on reaction mechanisms, determination of configurations, and practical syntheses of optically active compounds have been emphasized [1]. On the other hand, in order to explore reaction paths which are impossible with thermal reactions, the study of asymmetric photochemistry [2] or photochemistry with enantiodifferentiating sensitizers [3] has been developed. Recently, photochromic molecules with a chiral substituent [4–6] or those changing chirality with circularly polarized light [7] have been designed in order to apply to photo-optical switching or optical data storage of liquid crystals.

These molecules are designed to obtain large changes in optical properties of a liquid crystal, i.e., the purpose of these attempts is to control birefringence or rotational angle of polarization of linearly polarized light by a cholesteric pitch change induced by a photochemical change in molecular chirality or helical structure of the dopant. The most important point about dopant molecules is to earn change in chirality and interaction between the dopant and liquid crystal by photochemical reaction. That is different from usual photochromic reaction.

Sulfoxides are known to have pyramidal structure. Chiral center of sulfoxides is a sulfur atom combined with two substituents and oxygen atom and containing a lone pair. Sulfoxides are widely used as chiral auxiliaries [8]. Diaryl or alkyl aryl sulfoxides are known to undergo racemization at about 200°C which is believed to be due to thermal pyramidal inversion [9]. Since the activation energies of the thermal inversion are large, thermal inversion of sulfoxides do not occur at room temperature.

It is known, however, that diaryl or alkyl aryl sulfoxides undergo photoinversion reaction [10]. In our previous work, (R)-(+)-1-pyrenyl 4-tolyl sulfoxide was synthesized, and its photoracemization was confirmed to proceed in the same

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efficiency in polymer matrices at room temperature as in solution [11]. The reaction pathway has not been elucidated in details. We can assume three different mechanisms of the photoinversion: (1) Photoinversion occurs with the same mechanism as thermal inversion by using the energy produced by thermal deactivation from the excited state. (2) Photoinversion occurs through structural change of sulfinyl group in the excited state. (3) Photoinversion results from the recombination of radicals produced by photocleavage of C–S bond. Mechanism (1) does not hold true in case of a reaction in solution, because heat on molecules usually diffuses to solvent molecules very rapidly before the chemical reaction occurs. The possibility of mechanism (3) is discussed at the end of this paper. Briefly, since the photoinversion reaction occurs in higher efficiency than the photolysis [11], probably there should exist another reaction path of photoinversion besides radical-pair recombination mechanism. Since mechanism (2) seems most plausible, excited states and photophysical process of sulfoxides should be investigated in order to make the mechanism of photoinversion clear.

Photo-induced change in chirality is potentially applicable to photo-optical switching by using pitch change of cholesteric liquid crystals. Consequently, it is very important to investigate mechanisms of photoinversion reaction of sulfoxides. In the present paper, our aim is to investigate mechanisms of photoinversion reaction of sulfoxides by calculating electron density distribution of various excited states and measuring quantum yields of photoinversion, photolysis and fluorescence for aryl 4-tolyl sulfoxides substituted with several sizes of aromatic rings, and by considering the effects of solvent polarity and excitation energies on them. The measurements of CD spectra, HPLC and fluorescence spectra have been carried out.

The photochemistry of sulfoxides has not received much attention compared to that of other chromophores. A variety of photochemical reactions of sulfoxides are known to be initiated by homolytic C–S bond cleavage [12]. Then reaction pathways of the resulting radical pair and their complicated products were studied with ESR or CIDNP technique [13,14]. Since photochemical reactions of sulfoxides also proceed with high efficiency with a triplet sensitizer [15], excited triplet states of sulfoxides have been thought to play an important role. However, there are few studies of the excited triplet states. Jenks et al. measured spectra, quantum yields, life times and polar effect of phosphorescence of several phenyl or substituted phenyl sulfoxides in organic glass [16]. Although fluorescence was not observed like in case of aromatic ketones and triplet energies were a little higher than those of corresponding ketones, quantum yields of phosphorescence are very low. They observed a large blue shift of phosphorescence in a polar matrix. Due to the small quantum yields of phosphorescence even at low temperatures (<0.05), it is not clear whether deactivation from the excited singlet state occurs with high efficiency or deactivation from the excited triplet state after high efficiency intersystem crossing occurs with high efficiency. The study on the effects of π–π^* excited states by changing size of aromatic rings has not yet been carried out. So, in the present study we have measured fluorescence and photoinversion reactions of several sulfoxides of different ring sizes with the effects of conjugation of aromatic rings and polarity of solvents. From these results, we discuss the mechanisms of photoinversion and the excited states of sulfoxides by considering π–π^* and the other states.

2. Experimental

2.1. Materials

(S)-(−)-Phenyl 4-tolyl sulfoxide (PHSO), (R)-(+)-1-naphthyl 4-tolyl sulfoxide (NASO), (R)-(+)-9-phenanthryl 4-tolyl sulfoxide (PNSO) and (R)-(+)-1-pyrenyl 4-tolyl sulfoxide (PYSO) were prepared by Andersen's method [11,17] from (1S, 2R, 5S)-(+)-menthyl-(R)-*p*-toluenesulfinate and appropriate Grignard reagents provided from aromatic bromides and magnesium in anhydrous tetrahydrofuran. Products were purified by column chromatography and recrystallization. Optical purity was determined with chiral HPLC (Daicel Chiralcel OD). The pyramidal structures of aryl 4-tolyl sulfoxides (PHSO, NASO, PNSO and PYSO) are shown in Fig. 1.

2.1.1. (S)-(−)-phenyl 4-tolyl sulfoxide (PHSO)
^{1}H NMR ($CDCl_3$): δ 7.2 (d, 2H, tolyl-H), 7.6 (d, 2H, tolyl-H), 7.4–7.5 (m, 3H, phenyl-H), 7.5–7.6 (d, 2H, phenyl-H), 2.3 (s, 3H, Ar-CH_3). $[\alpha]^{20}_{405\,nm} = -25°$ (c 1.02, acetone). IR (KBr): 1046 cm^{-1}; S=O, 1495, 1595 cm^{-1}; aromatic C–C, 3050 cm^{-1}; aromatic C–H. Enantiomer excess (ee) $\geq$ 99%.

2.1.2. (R)-(+)-1-naphthyl 4-tolyl sulfoxide (NASO)
^{1}H NMR ($CDCl_3$): δ 7.2 (d, 2H, tolyl-H), 7.6 (d, 2H, tolyl-H), 7.5 (m, 2H, naphthyl-H), 7.6–7.7 (t, 1H, naphthyl-H),

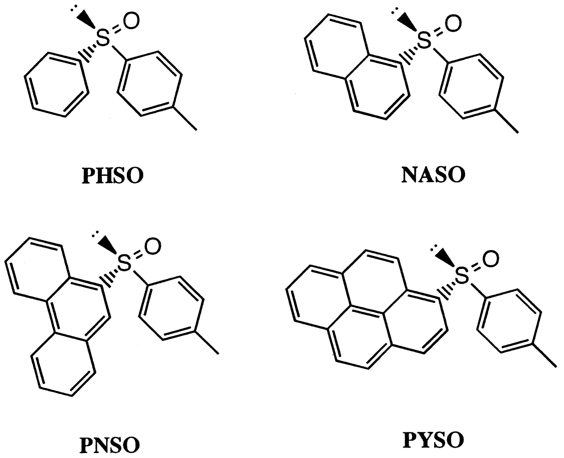

Fig. 1. Chemical structures of aryl 4-tolyl sulfoxides.

7.9–8.0 (m, 2H, naphthyl-$\underline{\mathrm{H}}$), 8.1–8.3 (m, 2H, naphthyl-$\underline{\mathrm{H}}$), 2.3 (s, 3H, Ar-C$\underline{\mathrm{H}}_3$). $[\alpha]^{20}_{405\,\mathrm{nm}} = +397°$ (c 2.07, acetone). IR (KBr): 1042 cm^{-1}; S=O, 1503, 1590 cm^{-1}; aromatic C–C, 3050 cm^{-1}; aromatic C–H. ee $\geq$ 99%.

2.1.3. (R)-(+)-9-phenanthryl 4-tolyl sulfoxide (PNSO)

^{1}H NMR (CDCl$_3$): δ 7.2 (d, 2H, tolyl-$\underline{\mathrm{H}}$), 7.6 (d, 2H, tolyl-$\underline{\mathrm{H}}$), 7.5–7.8 (m, 4H, phenanthryl-$\underline{\mathrm{H}}$), 8.1 (t, 2H, phenanthryl-$\underline{\mathrm{H}}$), 8.6–8.7 (m, 3H, phenanthryl-$\underline{\mathrm{H}}$), 2.3 (s, 3H, Ar-C$\underline{\mathrm{H}}_3$). $[\alpha]^{20}_{405\,\mathrm{nm}} = +36°$ (c 2.02, acetone). IR (KBr): 1050 cm^{-1}; S=O, 1492, 1591 cm^{-1}; aromatic C–C, 3032 cm^{-1}; aromatic C–H. ee $\geq$ 99%.

2.1.4. (R)-(+)-1-pyrenyl 4-tolyl sulfoxide (PYSO)

^{1}H NMR (CDCl$_3$): δ 7.2 (d, 2H, tolyl-H), 7.6 (d, 2H, tolyl-$\underline{\mathrm{H}}$) 8.1–8.6 (m, 9H, pyrenyl-$\underline{\mathrm{H}}$), 2.3 (s, 3H, Ar-C$\underline{\mathrm{H}}_3$). $[\alpha]^{20}_{405\,\mathrm{nm}} = +915°$ (c 0.70, acetone). IR (KBr): 1046 cm^{-1}; S=O, 1493, 1593 cm^{-1}; aromatic C–C, 3042 cm^{-1}; aromatic C–H. ee = 98.8%.

2.2. Fluorescence measurements

All solvents used for the measurements were of spectroscopic grade and used without further purification. Argon gas was bubbled through sample solutions in 1 cm × 1 cm quartz cell before measurements. The fluorescence quantum yields, Φ_{fl}, were obtained by comparison of the area of fluorescence spectrum (measured by Hitachi 850 fluorescence spectrophotometer) of a sulfoxide solution with that of 9,10-diphenylanthracene in cyclohexane ($\Phi_{\mathrm{fl}} = 1.0$; 262 nm excitation) [18]. The area of the spectrum was divided by optical density at the excitation wavelength before comparison. Fluorescence lifetime was measured by Hamamatsu C4780 sub-nanosecond single photon counting apparatus with a pulsed nitrogen laser (Laser Photonics LN120C2).

2.3. Photoracemization and photodecomposition

Sample solutions were degassed with argon bubbling or freeze-pump-thaw cycle before use and irradiated at appropriate wavelengths with 150 W Xe lamp through a monochromator (slit width 1 mm) and an optical quartz lens. Light intensity at 560 nm was measured with an optical powermeter (Advantest TQ8210). From wavelength distribution of Xe lamp intensity, relative transmittance of the monochromator, and sensitivity of the optical powermeter, absolute light intensity at the irradiated wavelengths was calculated. Reaction rates were measured from the changes in CD spectra (Jasco J-500A spectropolarimeter). In order to detect the reaction rates of photolysis, the changes in concentration of sulfoxides in the irradiated solutions were measured with HPLC (Wakosil 5SIL, eluent *n*-hexane, 2-propanol; 19 : 1).

3. Results and discussion

3.1. MO calculations

Since excited states of sulfoxides have not been characterized previously, electronic structures and transition energies of excited states of sulfoxides were calculated using configuration interaction singles (CIS) method with Dunning's valence double zeta basis set. The molecular structure of the ground state used in these calculations was determined by using Hartree–Fock method with STO-3G basis set. All the calculations were carried out with Gaussian 94 program. From the results of calculations for the electronic structures of ground states and excited states, it was shown that there are π–π^* (aromatic ring), n–σ^* (sulfinyl group) and π–σ^* (sulfinyl group) states in low-lying excited states of aromatic sulfoxides. Transition energies of excited singlet states, ΔE, and oscillator strengths, f, of each excited states are listed in Table 1. Although CIS transition energies are not very accurate enough to compare with the experimental data, it was shown that the transition energy of π–π^* decreases as the size of aromatic ring increases, while those of n–σ^* and π–σ^* do not decrease so much. Since the oscillator strength, f, of n–σ^* and π–σ^* are very small, these transitions are supposed to be forbidden. Jenks et al. [16] reported weak phosphorescence of aromatic sulfoxides in organic glass at 77 K and large blue shift of phosphorescence in polar matrix and referred that the dipole moment of the lowest excited triplet state is reduced by the charge transfer from the oxygen atom. It would be concluded that the lowest excited triplet states in these sulfoxides substituted with small aromatic rings are $^3(\mathrm{n}-\sigma)^*$ state.

Table 1
Calculated excited states, transition energies, ΔE and oscillator strength, f, of PHSO, NASO, PNSO and PYSO

Sulfoxide	Excited state	Singlet state		Triplet state
		ΔE (eV)	f	ΔE (eV)
PHSO	π–σ^*	3.69	0.0012	2.26
	n–σ^*	3.89	0.0025	2.50
	π–π^*	6.26	0.0670	3.45
	π–π^*	6.34	0.0623	3.46
NASO	π–σ^*	3.64	0.0011	2.22
	n–σ^*	3.24	0.0029	2.44
	π–π^*	5.47	0.1915	2.79
	π–π^*	5.62	0.0064	3.44
PNSO	π–σ^*	3.62	0.0022	2.20
	n–σ^*	3.89	0.0032	2.50
	π–π^*	5.24	0.0566	2.79
	π–π^*	5.37	0.0043	3.43
PYSO	π–σ^*	3.65	0.0010	2.23
	n–σ^*	3.84	0.0040	2.36
	π–π^*	4.79	0.5601	2.45
	π–π^*	4.97	0.0045	3.44

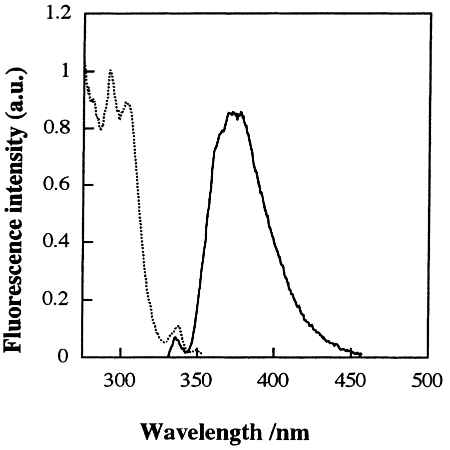

Fig. 2. Fluorescence specturm excited at 305 nm (solid line) and excitation spectrum monitored at 375 nm (dotted line) for 3.06×10^{-6} M PNSO in methanol.

3.2. Fluorescence measurements

Fluorescence spectra of PYSO could be observed in both methanol and hexane solutions. Although PNSO in methanol showed weak fluorescence, PNSO in hexane showed no fluorescence. No fluorescence spectrum was observed for PHSO or NASO solution in either methanol or hexane. Fluorescence spectra and excitation spectra of PNSO and PYSO in methanol are shown in Figs. 2 and 3, respectively. Quantum yields of fluorescence excited at several excitation wavelengths, Φ_{fl}, are listed in Table 2. Since the excitation spectra of both PNSO and PYSO are almost the same as their UV spectra in shape, it seems that there is no wavelength dependence in Φ_{fl} and small difference in Φ_{fl} for each sample is due to the experimental error.

Though fluorescence spectrum was not observed for sulfoxides with small aromatic rings and low conjugation (PHSO, NASO), fluorescence could be observed for sulfoxides with large aromatic rings and high conjugation (PNSO, PYSO). Moreover, the quantum yield of fluorescence for PYSO in methanol ($\Phi_{fl} = 0.03$) is about 10 times larger than that for PNSO in methanol ($\Phi_{fl} = 0.002$). As to the influence of solvent polarity, we could observe fluorescence of PNSO only in the polar solvent (methanol). The quantum yield of fluorescence for PYSO in methanol ($\Phi_{fl} = 0.03$) is about 10 times larger than that in hexane ($\Phi_{fl} = 0.002$). These characteristic tendencies of fluorescence of sulfoxides are the same as those of aromatic ketones or aromatic aldehydes [20]. From the fact that the values of Φ_{fl} of sulfoxides are very small and fluorescence of sulfoxides indicates the same tendencies as that of ketones as to the size effect of the aromatic rings, the quantum yields of intersystem crossing are suggested to be large. But the possibility of thermal deactivation from the excited singlet state to the ground state cannot be excluded.

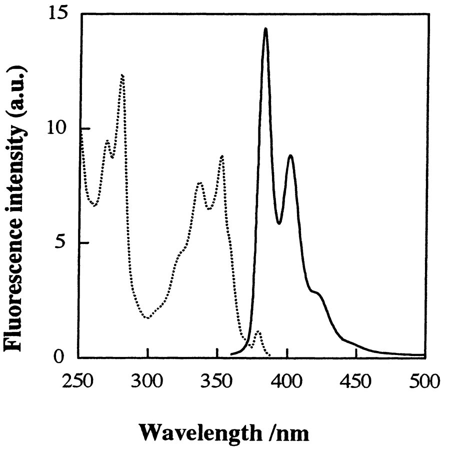

Fig. 3. Fluorescence spectrum excited at 350 nm (solid line) and excitation spectrum monitored at 400 nm (dotted line) for 6.75×10^{-6} M PYSO in methanol.

Table 2
Fluorescence quantum yields of PNSO in methanol and PYSO in methanol and hexane

Sample	Solvent	Excitation wavelength (nm)	Quantum yields Φ_{fl}
PNSO	Methanol	305	0.0017
		315	0.0017
PYSO	Methanol	337	0.035
		352	0.030
		360	0.022
PYSO	Hexane	337	0.0017
		352	0.0015
		360	0.0024

In the case of aromatic ketones and aromatic aldehydes, the π–π^* transition energy decreases as the conjugation of aromatic rings increases. However, the n–π^* transition energy is known to be constant in the first approximation, regardless of conjugation [21]. Since the efficiency of intersystem crossing from $^1(n-\pi)^*$ state is almost 100%, molecules whose lowest excited singlet state is $^1(\mathrm{n}-\pi)^*$ show no fluorescence. Consequently aromatic ketones and aromatic aldehydes whose aromatic rings are small do not show fluorescence but those whose aromatic rings are large show fluorescence owing to the change in the lowest excited singlet state from $^1(\mathrm{n}-\pi)^*$ to $^1(\pi-\pi)^*$ [20]. It is not known whether excited singlet states of sulfoxides change mainly to triplet states by intersystem crossing or to ground states by thermal deactivation. Our present results show that PNSO (methanol solution) and PYSO show fluorescence and quantum yield of fluorescence of PYSO (methanol solution) is larger than that of PNSO (methanol solution), while PHSO and NASO show no fluorescence. These results would be well explained in a similar manner to the cases in ketones and aldehydes, i.e., by the change in the lowest excited states from n–σ^* or π–σ^* to π–π^* with increasing degree of conjugation of aromatic rings and no fluorescence emission from $^1(\mathrm{n}-\sigma)^*$ or $^1(\pi-\sigma)^*$ state due to forbidden transition.

It is known that absorption band of n–π^* shifts to blue region and that of π–π^* shifts to red region in polar solvents. This is because the excitation energy of n–π^* transition increases but that of π–π^* transition decreases in polar solvents. When n–π^* transition energy and π–π^* transition energy are very close, aromatic aldehydes which do not emit fluorescence in non-polar solvents emit fluorescence in polar solvents [20].

As to the solvent effect on excited states of sulfoxides, it is supposed that, from the change in the dipole moment from the ground state to $^1(\mathrm{n}-\sigma)^*$ state, the transition energies, ΔE, of $^1(\mathrm{n}-\sigma)^*$ might increase in polar solvents. However, no blue shift in polar solvents was recognized for all peaks of UV spectra of all sulfoxides (PHSO, NASO, PNSO and PYSO). Consequently, absorption of n–σ^* cannot be characterized, and experimental value of transition energies of $^1(\mathrm{n}-\sigma)^*$ are not known. The facts that fluorescence from PNSO was observed only in methanol and emission from PYSO is stronger in methanol can be explained by assuming that π–π^* transition energies become close to the n–σ^* transition energy of the sulfoxides. It is known that fluorescence intensity of non-substituted pyrene is higher in non-polar solvents [19]. This characteristic of fluorescence of pyrene is opposite to that of PYSO.

In summary, there are two tendencies in the presently observed results: (1) fluorescence intensity increases as the π–π^* transition energy decreases, (2) fluorescence intensities from sulfoxides are higher in the polar solvent. These tendencies can be well explained by proposing that the π–π^* transition energy decreases with the increase in the size of aromatic rings, the π–π^* state becomes the lowest excited singlet state for PYSO, and the transition energies, ΔE, of $^1(\mathrm{n}-\sigma)^*$ increases in polar solvents. Although we could not observe n–σ^* or π–σ^* absorption directly, the experimental results in accordance with the calculated results that there are n–σ^*, π–σ^* and π–π^* states and the transition energy of π–π^* decreases as the size of aromatic ring increases, while those of n–σ^* and π–σ^* do not decrease so much. Although the existence of π–σ^* was not observed explicitly in fluorescence measurements, existence of π–π^* and n–σ^* and their effects on Φ_{fl} have been ascertained in the present work.

3.3. *Quantum yields of photoinversion and photolysis*

The decrease in the peak of CD spectra of PYSO in hexane solution during light irradiation is shown in Fig. 4. This decrease in optical activity means photoracemization of sulfoxide due to the photoinversion reaction and a small amount of photolysis. The reaction rates of the individual chiral sulfoxides in solution during irradiation are expressed as follows [11],

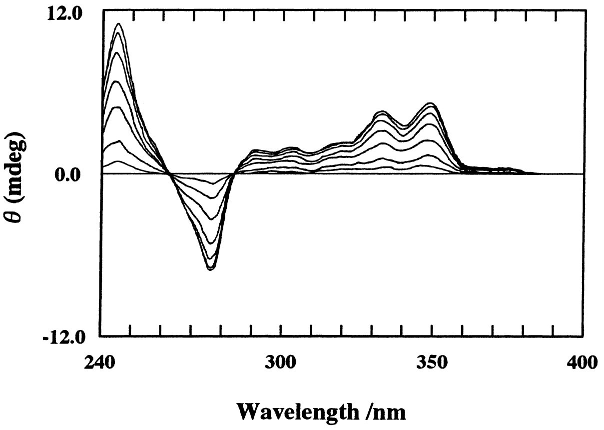

Fig. 4. The change in CD spectra of PYSO in hexane (concentration $C_0 = 5.33 \times 10^{-6}$ M) during light irradiation at 352 nm.

$$-\frac{\mathrm{d}C_\mathrm{R}(t)}{\mathrm{d}t}S\ell\times 10^{-3}=\{A_\mathrm{R}(t)\Phi_\mathrm{inv}-A_\mathrm{S}(t)\Phi_{inv}+A_\mathrm{R}(t)\Phi_\mathrm{dec}\}S \tag{1}$$

$$-\frac{\mathrm{d}C_\mathrm{S}(t)}{\mathrm{d}t}S\ell\times 10^{-3}=\{A_\mathrm{S}(t)\Phi_\mathrm{inv}-A_\mathrm{R}(t)\Phi_\mathrm{inv}+A_\mathrm{S}(t)\Phi_\mathrm{dec}\}S \tag{2}$$

$$A_\mathrm{R}(t)=I_0\left\{\left(1-10^{-\mathrm{OD}}\right)\frac{C_\mathrm{R}(t)}{C_0}\right\} \tag{3}$$

$$A_\mathrm{S}(t)=I_0\left\{\left(1-10^{-\mathrm{OD}}\right)\frac{C_\mathrm{S}(t)}{C_0}\right\} \tag{4}$$

$$C_\mathrm{R}(t)-C_\mathrm{S}(t) = C_0\exp\left\{-\frac{I_0(1-10^{-\mathrm{OD}})(2\Phi_\mathrm{inv}+\Phi_\mathrm{dec})\times 10^3}{C_0\ell}t\right\} \tag{5}$$

where I_0 is the number of irradiated photons per unit time and unit cross-section, S is the area of the irradiated cross section, $C_\mathrm{R}(t)$ and $C_\mathrm{S}(t)$ are the concentration of sulfoxides of R and S configuration, respectively, C_0 is the initial concentration, ℓ is the thickness of the system, $A_\mathrm{R}(t)$ and $A_\mathrm{S}(t)$ are the numbers of photons per unit time and unit cross-section which sulfoxides of R and S configuration absorb, respectively, Φ_inv and Φ_dec are the quantum yield of photoinversion reaction and photolysis, respectively, and t is the time. It is obvious that the quantum yields of photoinversion reaction and photolysis for sulfoxides of R configuration and S configuration are equal because of symmetry.

Changes in ellipticity, $\theta(t)$, were converted to the first-order plots (Fig. 5). The quantum yields of photoinversion reaction, Φ_inv, were obtained from the slopes of the first-order plots, together with the values of irradiated light intensity and Φ_dec (Eq. (12)). Ellipticity, $\theta(t)$, is expressed by the following Eqs. (6)–(12) [11],

$$\theta = 33\times\Delta\mathrm{OD} \tag{6}$$

$$\Delta\varepsilon=\varepsilon_\mathrm{lR}-\varepsilon_\mathrm{rR}=\varepsilon_\mathrm{rS}-\varepsilon_\mathrm{lS} \tag{7}$$

$$\mathrm{OD}_\mathrm{l}(t)=\left\{\varepsilon_\mathrm{lR}C_\mathrm{R}(t)+\varepsilon_\mathrm{lS}C_\mathrm{S}(t)+\frac{\varepsilon_\mathrm{lR}+\varepsilon_\mathrm{lS}}{2}C_\mathrm{d}(t)\right\}\ell \tag{8}$$

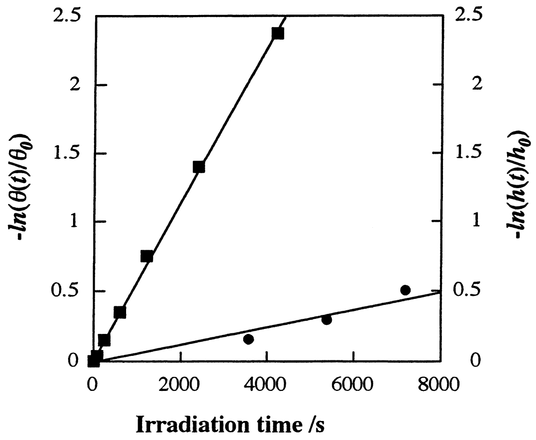

Fig. 5. The first-order plots for photoracemization (■) and photolysis (●) of PYSO in hexane.

$$\mathrm{OD_r}(t) = \left\{\varepsilon_{\mathrm{rR}} C_{\mathrm{R}}(t) + \varepsilon_{\mathrm{rS}} C_{\mathrm{S}}(t) + \frac{\varepsilon_{\mathrm{rR}} + \varepsilon_{\mathrm{rS}}}{2} C_{\mathrm{d}}(t)\right\}\ell \tag{9}$$

$$\Delta\mathrm{OD}(t) = \mathrm{OD_l}(t) - \mathrm{OD_r}(t) = \Delta\varepsilon\{C_{\mathrm{R}}(t) - C_{\mathrm{S}}(t)\}\ell \tag{10}$$

$$C_{\mathrm{R}}(t) - C_{\mathrm{S}}(t) = \frac{\Delta\mathrm{OD}(t)}{\Delta\varepsilon\ell} = \frac{\theta(t)}{33\Delta\varepsilon\ell} \tag{11}$$

$$\ln\left\{\frac{\theta(t)}{\theta_0}\right\} = -\frac{I_0(1 - 10^{-\mathrm{OD}})(2\Phi_{\mathrm{inv}} + \Phi_{\mathrm{dec}}) \times 10^3}{C_0\ell}t \tag{12}$$

where $\varepsilon_{\mathrm{lR}}$, $\varepsilon_{\mathrm{rR}}$, $\varepsilon_{\mathrm{lS}}$ and $\varepsilon_{\mathrm{rS}}$ are the molar extinction coefficients of the sulfoxide of R configuration for left-circularly-polarized light (l-CPL) and right-circularly-polarized light (r-CPL) and that of S configuration for l-CPL and r-CPL, respectively, and $C_{\mathrm{d}}(t)$ is the concentration of by-products of photolysis. Upon preparing Eqs. (8) and (9), we assumed that total loss of sulfoxide during irradiation is equal to the amount of by-products which absorb the irradiated light with the same molar extinction coefficients as the sulfoxide. From the wavelength distribution of Xe lamp intensity, that of relative transmittance of monochromator and that of sensitivity of optical powermeter, absolute light intensity at the irradiated wavelengths was calculated. Irradiated light intensity was converted to the number of irradiated photon, I_0, per unit time and unit cross-section. The concentrations of sulfoxides in solution both before, h_0, and at irradiation time t, $h(t)$, were measured with HPLC. Quantum yields of photolysis, Φ_{dec}, were estimated from the rate constants of photolysis (slopes of first-order plots in Fig. 5) and I_0, by using Eq. (13).

$$\ln\left\{\frac{h(t)}{h_0}\right\} = -\frac{I_0(1 - 10^{-\mathrm{OD}})\Phi_{\mathrm{dec}} \times 10^3}{C_0\ell}t \tag{13}$$

The quantum yields, Φ_{inv}, and Φ_{dec}, found in the present work are listed in Table 3. The values of Φ_{inv} and Φ_{dec} for PHSO, NASO, and PNSO were estimated to be 0.3–0.4 and 0.03–0.05, respectively, irrespective of solvent polarity or irradiation wavelength. As to PYSO, Φ_{inv} was found to be 0.02–0.03 in both the solutions, while Φ_{dec} in methanol and hexane was 0.002–0.003 and 0.012–0.016, respectively.

Table 3
Quantum yields of photoinversion, Φ_{inv} and photolysis, Φ_{dec}, of aryl *p*-tolyl sulfoxides in methanol and hexane

Sample	Solvent	Excitation wavelength (nm)	Φ_{inv}	Φ_{dec}	$\Phi_{\mathrm{inv}}/\Phi_{\mathrm{dec}}$
PHSO	Methanol	270	0.33	0.037	8.96
	Hexane	270	0.34	0.047	7.16
NASO	Methanol	305	0.31	0.021	14.45
		320	0.32	0.028	11.12
	Hexane	305	0.30	0.041	7.21
		320	0.34	0.032	10.79
	Hexane*[a]	305	0.34	0.020	16.75
	Hexane*[b]	305	0.30*[c]		
PNSO	Methanol	305	0.35	0.029	11.99
		315	0.33	0.035	9.47
	Hexane	305	0.32	0.033	9.87
		315	0.34	0.038	8.92
	Hexane*[a]	305	0.33	0.034	9.74
	Hexane*[b]	305	0.33*[c]		
PYSO	Methanol	337	0.023	0.0028	8.25
		352	0.028	0.0028	9.86
		360	0.025	0.0030	8.33
		378	0.019	0.0023	8.20
	Hexane	337	0.031	0.011	2.75
		352	0.034	0.0083	4.05
		360	0.016	0.016	1.05
		378	0.019	0.016	1.23
	Hexane*[a]	352	0.031	0.014	2.31
	Hexane*[b]	352	0.035*[c]		

[a] Degassed by freeze-pump-thaw cycle.
[b] Contains 1 M piperylene.
[c] The value of $\Phi_{\mathrm{inv}} + (1/2)\Phi_{\mathrm{dec}}$.
Experimental errors for Φ_{inv} and Φ_{dec} are within 30%.

Since the lowest excited triplet states for sulfoxides with small aromatic rings were concluded to be $^3(\mathrm{n} - \sigma)^*$ as discussed before, it is supposed that lowest excited singlet state of PHSO is $^1(\mathrm{n} - \sigma)^*$ state. Due to no fluorescence for NASO, the lowest excited singlet for NASO also seems to be $^1(\mathrm{n} - \sigma)^*$ state. PNSO shows very weak fluorescence in methanol, so its lowest excited state seems to have π–π^* characteristics in some degree. Its lowest excited state, however, still has n–σ* characteristics because fluorescence spectrum is not shown in hexane. PYSO seems to have π–π^* characteristics in its lowest excited singlet because of its weak fluorescence spectra. The effect of the n–σ* state is shown in the solvent effect as discussed before. From the tendency of experimental results, photoinversion of sulfoxides whose lowest excited singlet state seems to have n–σ* characteristics proceeds with high efficiency, while photoinversion of those whose lowest excited singlet state shows π–π^* characteristics proceeds with relatively low efficiency. We suppose that electron transfer from the n orbital of an oxygen atom to the non-bonding σ* orbital of the sulfinyl group in n–σ* excited states induces a change in hybridization around the sulfur atom. This change in hybridization is expected to involve the change in a molecular shape from the pyramidal structure (sp^3) to the triangular-double-pyramidal structure (sp^3d) [22]. However, we cannot propose a good explanation for the mechanism of photoinversion if we might suppose that photoinversion occurred in π–σ* state. The inversion of a sulfoxide structure is supposedly produced during the change in electronic states from n–σ* state to the ground state. It is worthy to note that the ratio, Φ_{dec}/Φ_{inv}, stays almost constant with the values of 0.06–0.14 in all cases of the present experiments except for PYSO in hexane.

The photoinversion reaction of PHSO is expected to occur either during a deactivation from an $^1(n-\sigma)^*$ state to the ground state or during a change from an $^3(n-\sigma)^*$ state to the ground state after an intersystem crossing from the $^1(\mathrm{n}-\sigma)^*$. Probably, photoinversion of NASO proceeds along almost the same photophysical processes as those of PHSO. PNSO is different from PHSO and NASO because of its fluorescence emission in methanol. As shown in small Φ_{fl} in methanol (~0.002) and no fluorescence in hexane, the lowest excited singlet state still seems to have strong characteristics of an n–σ* state. We think that the high efficiency of photoinversion for PNSO is due to strong n–σ* characteristics. On the other hand, we attribute low quantum yields of photoinversion for PYSO to its relatively stronger π–π* characteristics induced by the decrease in π–π* transition energy. A fluorescence lifetime of PYSO in methanol excited at 337 nm with a nitrogen laser was observed to be 2.0 ns. This value is much smaller than that of pyrene (450 ns in cyclohexane, 500 ns in ethanol [23]). Since both Φ_{inv} and Φ_{fl} are not so large, we can attribute this short-lived fluorescence emission not only to an intersystem crossing to $^3(n-\sigma)^*$ but also to an increase in the rates of an intersystem crossing to the $^3(\pi-\pi)^*, ^3(\pi-\sigma)^*$ or a thermal deactivation from an excited singlet state to the ground state. From the appearance of an absorption band of the 0–0 transition of the pyrenyl group (378 nm) in UV spectra of PYSO, it is recognized that the symmetry-forbidden 0–0 transition becomes an allowed transition by the presence of a sulfinyl group [11].

The excitation wavelengths did not affect Φ_{inv} and Φ_{dec}. This means that it is unable to excite a particular transition state or to change the reaction path by selecting the excitation wavelength. There is no difference in Φ_{inv} and Φ_{dec} between argon-bubbled samples and freeze-pump-thaw samples. The influence of the addition of 1 M piperylene on Φ_{inv} which is known as a triplet quencher was not observed either. It is shown that the photoinversion was not disturbed even in such conditions that triplet states are immediately and completely quenched. Although photoinversion and photolysis by triplet sensitizers have been reported [15], we cannot exclude the possibility that the reaction proceeds from the excited singlet state. Hence, it is supposed that the photoinversion is due to a structural change in the n–σ* state induced by the change in hybridization around the sulfur atom and proceeds during the change from the n–σ* state to the ground state irrespective of the multiplicity of the excited state. The photoinversion occurs during the change in electronic states from the n–σ* states to the ground state, but we cannot suggest whether photoinversion and photolysis proceed from the excited singlet state or the triplet state. Only in the case of PYSO in hexane, it is supposed that the photolysis occurs at a faster rate than in other cases probably due to a different mechanism.

3.4. Possibility of recombination mechanisms

The C–S bonds of sulfoxides are known to be cloven by light irradiation. If an aromatic ring is bonded to a sulfur atom directly, the cleavage is suppressed to some degree but not completely. A radical pair produced by the homolytic C–S bond cleavage forms a variety of photolysis products. There is a possibility that sulfoxides are also formed by radical recombination. Since the sulfoxides formed by the radical recombination are predicted to be racemic, they seem to be same as those produced by the photoinversion reaction. Consequently, we need to estimate the ratio of sulfoxides formed by the radical recombination.

Since benzyl radicals are stable, C–S bonds of benzyl sulfoxides are known to be cloven predominantly by light irradiation. So the photoinversion of benzyl sulfoxides proceeds through the radical recombination mechanism almost completely. The efficiency of photoinversion by the radical recombination mechanism can be estimated from experimental data of photoinversion and photolysis of benzyl sulfoxides measured by Jenks et al. [23].

Since the reaction paths of the radical pair are classified into four paths, escape, recombination which keeps stereospecificity, recombination which induces inversion, and recombination which produces by-products, the ratio of quantum yield of photoinversion, Φ_{inv}, to that of photolysis, Φ_{dec}, is expressed as follows:

$$\frac{\Phi_{inv}}{\Phi_{dec}} = \frac{k_{ri}}{k_{esc} + k_{rp}} \qquad (14)$$

where k_{ri}, k_{esc} and k_{rp} are the reaction rates of recombination involving inversion, escape, and recombination involving photolysis. Jenks et al. [24] reported the quantum yield of the loss of optical activity, $\Phi_{rot}(= 2\Phi_{inv} + \Phi_{dec})$, and that of photolysis, $\Phi_{loss}(= \Phi_{dec})$, of (+)-benzyl *p*-tolyl sulfoxide in acetone to be 0.41, 0.33, respectively. Φ_{inv} is obtained to be 0.04 from Φ_{rot} and Φ_{loss}. They also carried out the analysis of photolysis products of several aromatic sulfoxides [24,25].

From the values of Φ_{inv} and Φ_{dec} (=Φ_{loss}) obtained above, $k_{ri}/(k_{esc} + k_{rp})$ is estimated to be 0.12. The value of 0.23 for Φ_{inv}/Φ_{dec} was reported for the photolysis of benzyl *p*-tolyl sulfoxide in 2-propanol [23]. These values mean that the possibility of photoinversion in recombination mechanisms is about 20% of that of photolysis. In the present case, the proportion of photolysis is very small compared to photoinversion ($\Phi_{inv}/\Phi_{dec} = 10$ for most cases in Table 3), and moreover, the absolute values of Φ_{inv} for PHSO, NASO, and

PNSO (0.30–0.35) is much larger than $\Phi_{\mathrm{inv}} = 0.04–0.07$ for benzyl *p*-tolyl sulfoxide. From these estimations, it turns out that the quantum yields of Φ_{inv} found in this study would not be due to the photolysis and radical recombination mechanism.

4. Conclusion

Chiral aryl 4-tolyl sulfoxides which have different sizes of aromatic rings were prepared. The excited states of sulfoxides were characterized as n–σ* (sulfinyl group), π–σ* (sulfinyl group) and π–π* (aromatic ring) from MO calculation. In their fluorescence measurements, the effects of solvent polarity and degree of conjugation of aromatic rings show the same tendency as those of aromatic ketones. While π–π* transition energies decrease as the degree of conjugation increases, an n–σ* transition energy does not decrease so much. Quantum yields of photoinversion, Φ_{inv}, and photolysis, Φ_{dec}, for PHSO, NASO and PNSO were estimated to be 0.3–0.4 and 0.03–0.05, respectively. The values of Φ_{inv} for PYSO in methanol and hexane are 0.02–0.03 and Φ_{dec} for PYSO is 0.002–0.003 in methanol and 0.012–0.016 in hexane. Effects of the excitation wavelength or the addition of piperylene on Φ_{inv} and Φ_{dec} were not observed. We conclude that photoinversion occurs during the change from the n–σ* state to the ground state. A recombination path induced by C–S bond cleavage would make little contribution to the photoinversion of the present case.

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