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Unusual Fluorescence Spectroscopic Properties of 9-Anthrylethylene Derivatives: Photoisomerization

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The fluorescence spectroscopic properties of both *trans* and *cis* forms of 9-anthrylethylene derivatives such as 9-AnthCH=CHCO₂CH₃ [I] and 9-AnthCH=CHCN [II] as well as 9-AnthCH=CHCH₂O₂CCH₃ [III] and 9-AnthCH=CHCH₂OH [IV] have been measured in various solvents. In nonpolar solvent, the *trans*-I and *trans*-II show dual emission spectral bands at 340 nm and 460 nm when exciting with 270 nm while the other *trans* derivatives show single emission band at 430 or 460 nm. The dual emissions exhibit different excitation spectra, indicating that two emissive states are different from each other. It is interesting to note that the 340 nm emission of both *trans*-I and *trans*-II is enhanced at the expense of the drastic quenching of the 460 nm emission as the solvent polarity increases. The dual emissions are also observed for both *cis*-I and *cis*-II. The solvent dependence of the fluorescence decay times and quantum yields can be correlated with the solvent and excitation wavelength dependences of the *trans*→*cis* photoisomerization quantum yields. These results indicate that the 340 nm emission is originated from the S₂ state of the *cis*-form, and the S₁ state is the only singlet excited state presenting a large CT (charge transfer) character to facilitate the photoisomerization.

Introduction

The mechanism and the potential energy surfaces of *cis*-

trans isomerization of olefines have been actively investigated since the extensive works for the sensitized isomerization of stilbenes by Hammond, Saltiel, and co-workers in 1960s.¹⁻⁶ As a result it was revealed that stilbene undergoes mutual isomerization between *cis* and *trans*

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isomers in the singlet or triplet manifold on direct irradiation or triplet sensitization, respectively. It had long been accepted that the olefines generally would undergo isomerization mutually between their *cis* and *trans* isomers by experimental and theoretical works.¹⁻¹⁴

In 1983, a series of 1-substituted and 1,1-disubstituted 2-(9-Anthryl)alkenes were synthesized and investigated in terms of spectroscopic properties and photoisomerizations by Becker and Andersson.¹⁵ As a result large Stokes shifts of up to 10,000 cm⁻¹ between absorption and emission maxima are attributed to geometrical differences between the ground state and emitting excited state. The [*cis*]:[*trans*] ratio of the photostationary state was found to depend markedly on the nature of the 1-substituent. Photochemical isomerization of 1,3- and 1,5-bis(9-anthryl)-substituted *trans* olefines results in the formation of intramolecular [4 π +4 π] or [4 π +2 π] cycloaddition products. The cycloaddition reactions of carbonyl-substituted anthracenes are suggested to involve the triplet excited state.

However, in 1983 Arai *et al.* reported that substitution of an anthracene nucleus on a C=C double bond led to a novel one-way isomerization, taking place solely from the *cis* isomer to the *trans* isomer through a quantum chain process resulting in 100% *trans* isomer by photoisomerization.¹⁶ This one-way isomerization takes place as an adiabatic process in the triplet manifold on direct irradiation as well as on triplet sensitization. That is, one-way isomerization revealed to be a high quantum yield of isomerization (≥ 1) through *trans* triplet (³t*) while two-way isomerization appeared to be a low quantum yield of isomerization (≤ 0.5) through perpendicular triplet (3p*). The isomerization mode, one-way or two-way, of aromatic olefines in the triplet states is further revealed to be governed by the properties of the substituents on their ethylenic bonds. However, olefines (ArCH=CHR) having an aromatic group (Ar) with a low triplet energy (E_T) like anthracene (42.0 kcal mol⁻¹) undergo the one-way isomerization regardless of the substituents (R) on their ethylenic bonds. The quantum yield of the isomerization and T-T absorption spectra indicate ³t* is lower in energy than both ³c* and 3p* and, therefore, is the most stable conformation in the excited triplet state.

In 1992, Karatsu, Arai, Tokumaru and coworkers studied the triplet sensitized isomerization of 1- & 9-Anthryl-ethylene (AnthCH=CHBu', BA) and compared their behavior with that of 2BA.¹⁸ As the results, the T-T absorption spectra observed just after the laser excitation gradually shifted to that of *trans* isomers in the time scale of 100 ns. The barriers for ³c* \rightarrow ³t* conversion (E_a (³c* \rightarrow ³t*)) were 6.0, 4.6 and 3.1 kcal mol⁻¹, for 2BA, 1BA and 9BA, respectively. Thus, the value of E_a (³c* \rightarrow ³t*) decreases in the order of 2-, 1-, and 9-position, probably due to the stabilization of the triplet state through increased conjugation between the anthracene nucleus and the double bond.

In 1995, new 9-anthrylethylene derivatives I-IV (Scheme 1) were synthesized and investigated in terms of spectroscopic properties and photoisomerizations by Gopal, Reddy, and Rao.¹⁹ They observed dual fluorescence which was assigned to be originated from locally excited singlet state and charge transfer singlet excited state for I & II,

respectively. It is also suggested that the quantum chain photoisomerization takes place through singlet charge transfer excited state. An evidence for the quantum chain photoisomerization is that upon increasing of concentration of substrate, the quantum yield of isomerization is increased and the fluorescence intensity is quenched in hexane and methanol. Especially they suggested that the quenching of locally excited state fluorescence was involved in the energy transfer process to excite a ground state molecule.

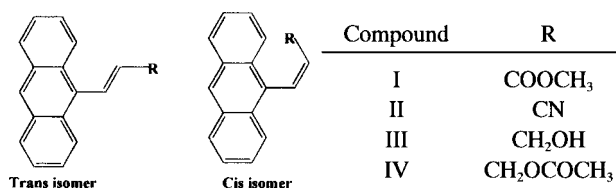
However, the evidences provided for the quantum chain photoisomerization seem to raise the following questions. i) Why does the isomerization take place by quantum chain process with low a quantum yield (≤ 0.5) in contrast to general quantum chain process? ii) Why doesn't *cis* \rightarrow *trans* isomerization take place on direct irradiation in spite of the fact that both *cis* and *trans* isomer form an excited charge transfer state. From this question, Rao *et al.*'s assignment for the dual fluorescence (local emission and charge transfer emission) seems to be wrong. Besides Rao *et al.* showed a conflicting concentration effect of substrate on the dual fluorescence in different concentration ranges. At lower concentration of substrate the charge transfer emission is enhanced at the expense of quenching of the locally excited state emission while the charge transfer emission is quenched at higher concentration. Thus, their conclusions that energy transfer from a singlet excited state to a ground state is involved in the quantum chain isomerization seems to be suspicious, and the concentration effects they observed is probably due to self-absorption.

For these reasons, we attempted to explore the fluorescence spectroscopic properties of 9-anthrylethylene derivatives in various solvents more systematically. The spectroscopic properties were discussed in relation to photoisomerization.

Experimental

Anthrylethylene derivatives I-IV (Scheme 1) were synthesized by use of the Horner-Wadsworth-Emmon reaction.^{20a} The *cis* isomer was either generated photochemically or synthesized.^{19,20b} The compound synthesized was purified by column chromatography. The structure and molecular weight of compound I-IV were characterized by ¹H NMR and ¹³C NMR and Mass spectra, respectively. All the solvents used were spectroscopic grades (Merck Co.) and used as received.

The absorption spectra were measured on a Cary 3E UV-VIS spectrophotometer. The steady-state fluorescence spectra were recorded on a scanning SLM AMINCO 4800 spectrofluorometer which makes it possible to obtain corrected spectra using Rhodamine B as a quantum counter.



Scheme 1. The molecular structure of 9-anthrylethylene derivatives (I-IV).

The solutions were accurately diluted with the proper solvent to have an optical density not to exceed 0.6 at the excitation wavelength to eliminate the self-absorption effect. The final concentration of solutions was 1×10^{-5} M. The 450W Hg Arc lamp was used for irradiation.

Fluorescence lifetimes of Anthrylethylene derivatives I & II in solutions were measured by a time correlated single photon counting (TCSPC) method. The excitation source was a tunable self-mode-locked Ti-sapphire laser (range from 820 to 930 nm) with a repetition rate of 8 MHz, a pulse width of ~ 200 fs. To excite sample, the laser pulse was frequency-doubled by β -BBO (β -barium borate) crystal (ca. 398 nm). For III & IV derivatives, the hydrogen flash arc lamp was used.

Results and Discussion

The absorption spectra of both *trans* and *cis* forms of 9-AnthCH=CHCO₂CH₃, [I] were measured in hexane as shown in Figure 1 (a). Both *cis*-I and *trans*-I showed dual absorption bands at 256 nm and 384 nm, but the absorption spectral features are slightly between *cis* and *trans* isomer, indicating that the conjugation between ethylene and anthracene moiety is decreased by the geometrical restraint of *cis* isomer. However, the absorption spectra of both *cis*-I and *trans*-I did not show any solvent effect, indicating that both *cis*-I and *trans*-I are not dependent on solvent polarity at the ground state. The similar results were observed for II-

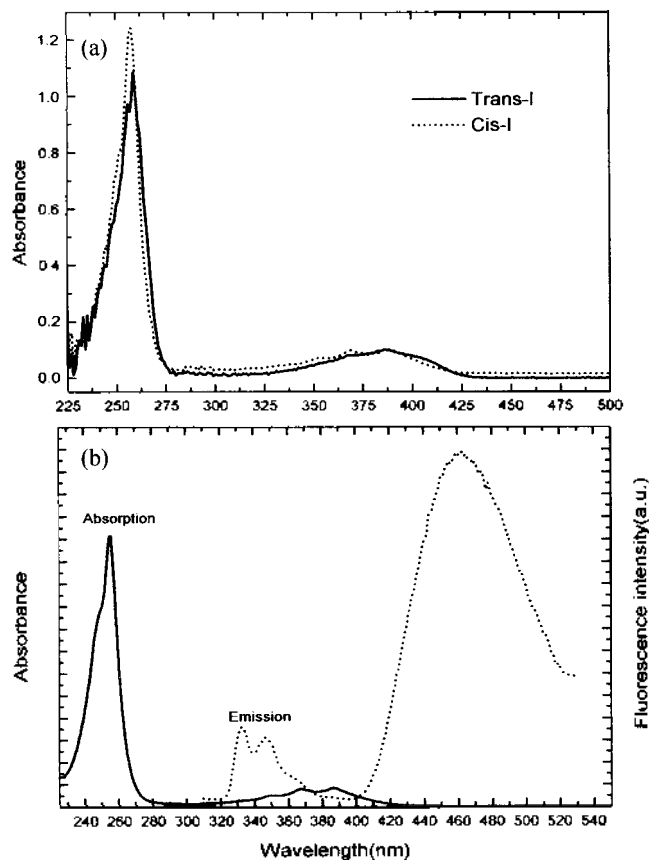


Figure 1. (a) Absorption spectra of *trans*-I and *cis*-I in hexane at room temperature (b) Absorption and Fluorescence emission spectra of *cis*-I in hexane at room temperature ($\lambda_{ex}=270$ nm).

IV compounds. In an attempt to further rationalize the differences on geometry between *cis* isomer and *trans* isomer, we have performed a theoretical optimized calculation on II derivative. The dihedral angle between ethylene and anthracene moiety for *cis* isomer and *trans* isomer is 91.28 degrees and 0 degree, respectively.

In contrast to the absorption spectra, there is a dramatic change in the fluorescence behavior of I and II in various solvents. In nonpolar solvent such as hexane, the *cis*-I shows significant dual emission spectral bands at 340 nm and 460 nm when exciting with 270 nm while the *trans*-I shows an almost single emission band at 460 nm with a weak emission at 340 nm as depicted in Figure 1 (b). However, both *cis*-II and *trans*-II derivatives show the dual emission spectral bands at 340 nm and 460 nm in nonpolar solvent when exciting with 270 nm as depicted in Figure 2. The dual emission maxima were observed to be red shifted by 20-40 nm in polar solvent indicating that the substrate is more polar in the excited state than in the ground state. It is interesting to note that the first emission maxima at 340 nm

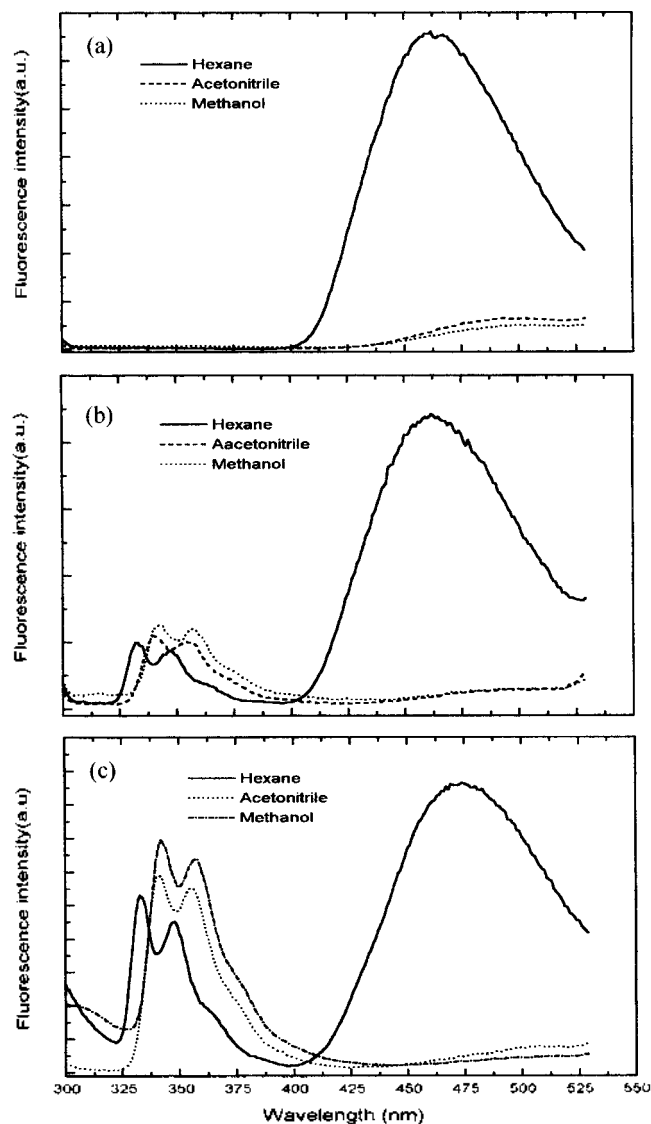


Figure 2. Fluorescence emission spectra of *trans*-I(a), *cis*-I(b) and *trans*-II(c) in various solvents ($\lambda_{ex}=270$ nm).

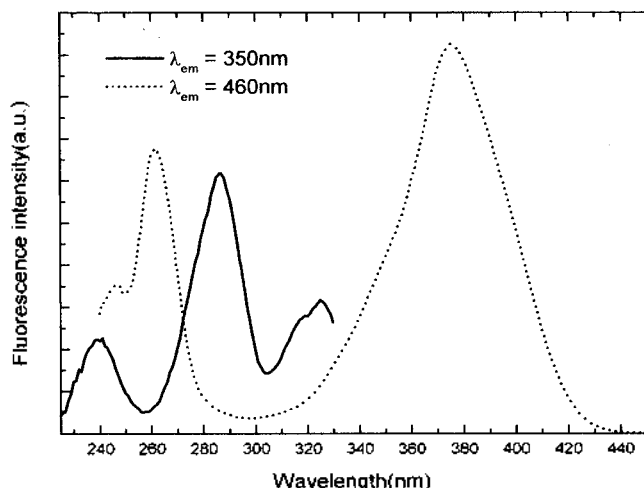


Figure 3. Fluorescence excitation spectra of *cis*-II in hexane.

observed from I and II derivatives are located at the shorter wavelength than the absorption maxima 384 nm. These emission maxima has not been observed by Rao *et al.*¹⁹ The dual emission exhibits different excitation spectra, indicating that the two emissive states are different from each other as depicted in Figure 3. It is interesting to note that the first emission of the *trans*-I and *trans*-II is enhanced at the expense of the drastic quenching of the second emission at 460 nm as the solvent polarity increases (see Figure 2). The weakly observed first emission of *trans*-I at 340 nm is observed to be significantly appeared by photoirradiation. These results indicate that the first emission observed from I and II is originated from the *cis* isomer formed by photoisomerization. However, the III and IV derivatives with electron-donating groups on ethylenic bond show only single emission band around 430 nm and did not undergo solvatochromic effect as shown in Figure 4. These results imply that the fluorescence spectroscopic properties of 9-anthrylethylene derivatives are markedly dependent on the nature of substituents on ethylenic bond.

For both I and II compounds, the fluorescence Stokes shift for the second emission is larger in polar solvent such as methanol than that in observed nonpolar solvent such as hexane. However, For both III and IV derivatives with an electron-donating group of ethylenic bond, the fluorescence Stokes shift is constant regardless of increasing of solvent polarity. The large Stokes shift of the second emission of both I and II in polar solvent should be due to the increase of dipole moments and polarities in the excited state as described above. This implies that the second emission is due to the formation of an excited state CT character, indicating that positive and negative charges become localized on anthracene moiety and electron-withdrawing groups on ethylenic bond, respectively. If the molecule-solvent interaction is primarily of a dipole-dipole characteristics, the Stokes shift ($\nu_a - \nu_f$) is dependent on the solvent polarity parameters (orientation polarizability, Δf) as expressed in the following Eq. (1),²¹

$$\nu_a - \nu_f = \frac{2}{hc} \times \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \times \frac{(\mu_e - \mu_g)}{a^3} + \text{constant}$$

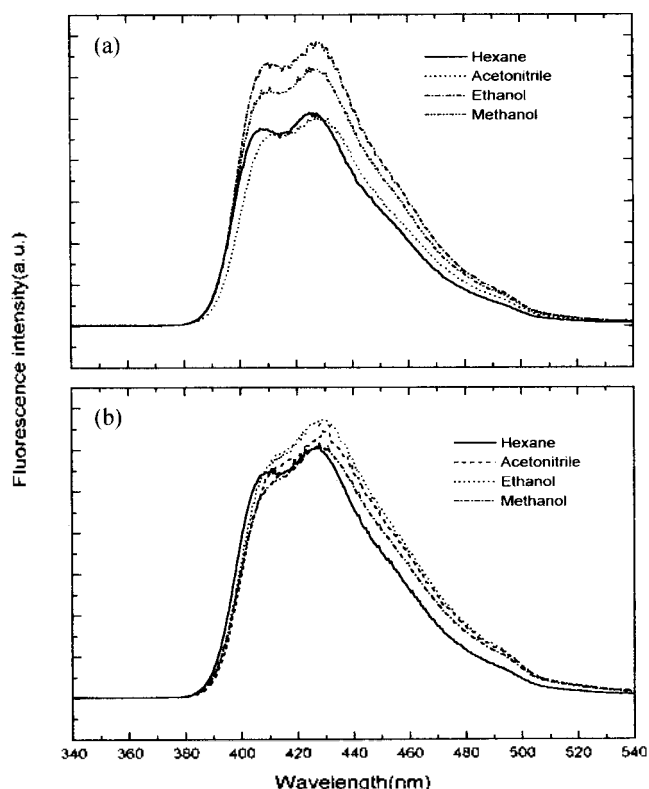


Figure 4. Fluorescence emission spectra of *cis*-III(a) and *cis*-IV(b) in various solvents.

$$\Delta f = \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \quad (1)$$

where n and ϵ is refractive index and dielectric constant of the solvent, respectively. h is Planck's constant, c is the speed of light, and a is the Onsager radius cavity. μ_e and μ_g are the excited state and the ground state dipole moment, respectively. Figure 5 shows the plot of $(\nu_a - \nu_f)$ vs. orientation polarizability (Δf). Clearly both I and II derivatives are more sensitive to solvent polarity than III and IV derivatives, indicating that the formation of the

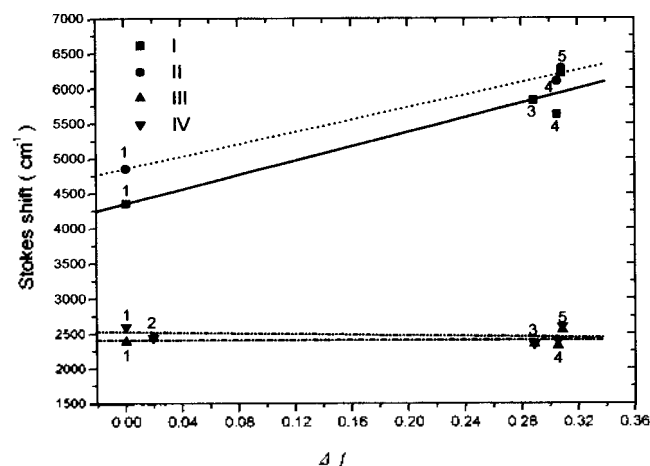


Figure 5. The Stokes shift of I, II, III & IV fluorescence as a function of solvent polarity parameters (1=hexane, 2=dioxane, 3=EtOH, 4=acetonitrile, 5=methanol).

excited-state CT character is largely dependent on the nature of substituents on ethylenic bond.

In order to further understand the fluorescence properties of both I and II, we have measured the fluorescence quantum yield and the fluorescence decay times of the 9-anthrylethylene derivatives in various solvents. Figure 6 shows the typical fluorescence decay for *trans*-II and *cis*-IV in various solvents. For II derivative, the lifetime of the second emission was found to be significantly decreased as the solvent polarity increases while the lifetime of the first emission is increased with increasing of solvent polarity (Table 1). These trends are also observed for the fluorescence quantum yield. However, for both III and IV derivatives, the fluorescence decay times are increased with increasing of solvent polarity and the fluorescence quantum yield show a constant value regardless of solvent polarity. The data analysis exhibits that the nonradiative rate constant (k_{nr}) for I and II derivatives is significantly increased with increasing of the solvent polarity while it is little changed for the III and IV derivatives. That is, for I and II derivatives the nonradiative rate constant (k_{nr}) is increased with increasing of solvent polarity, being consistent with the enhancement of photoisomerization. The fluorescence decay times and quantum yield can be correlated with the solvent dependences of the *trans*→*cis* photoisomerization quantum yield as shown in Table 1. The decrease of the fluorescence quantum yield and the fluorescence decay

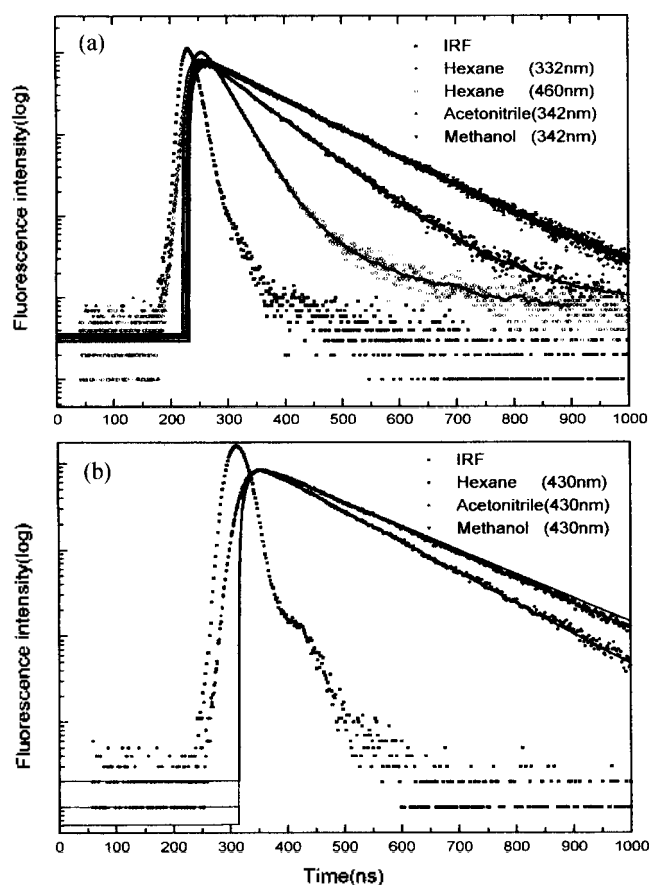


Figure 6. Fluorescence decay profiles of *trans*-II(a) and *cis*-IV (b) in Various solvents (λ_{exc} =270 nm) (The number in parentheses represents the monitoring wavelength).

Table 1. Absorption & fluorescence maxima, quantum yields (Φ_f & Φ_{i-c}), lifetimes (τ_f), radiative rate constants (k_f), and non-radiative rate constants (k_{nr}) of anthrylethylene derivatives in various solvents

Compd	Solvent	λ_{abs} (nm)	λ_{fluo} (nm)	Φ_f	τ_f (ns)	k_f	k_{nr}	Φ_{i-c}
<i>trans</i> -I	Hexane	256	332	-	-	-	-	-
		386	464	0.116	0.95	1.2×10^8	9.3×10^8	0.14
	Aceto-nitrile	256	342	-	-	-	-	0.20
	Methanol	256	342	-	-	-	-	-
		389	513	0.013	0.17	7.6×10^7	5.8×10^8	0.20
<i>cis</i> -I	Hexane	256	332	2.2×10^{-3}	-	-	-	-
		384	465	0.101	1.0	1.0×10^8	9.0×10^8	-
	Aceto-nitrile	256	342	2.2×10^{-3}	-	-	-	-
	Methanol	256	342	2.2×10^{-3}	-	-	-	-
		384	510	0.010	0.17	5.9×10^7	5.8×10^8	-
<i>trans</i> -II	Hexane	256	332	8.3×10^{-3}	81.4	1.0×10^5	1.2×10^7	0.19
		386	475	0.201	1.55	1.3×10^8	5.2×10^8	-
	Aceto-nitrile	256	342	8.5×10^{-3}	118.7	0.7×10^5	8.4×10^6	0.28
	Methanol	256	342	8.5×10^{-3}	123.1	0.7×10^5	8.1×10^6	-
		389	515	0.020	0.25	8.0×10^7	3.9×10^8	0.23
<i>cis</i> -III	Hexane	256	428	0.66	113.6	5.8×10^6	3.0×10^6	-
		386	428	0.64	151.6	4.2×10^6	2.4×10^6	-
	Methanol	256	428	0.65	155.0	4.2×10^6	2.3×10^6	-
		386	428	0.65	155.0	4.2×10^6	2.3×10^6	-
<i>cis</i> -IV	Hexane	256	430	0.97	120.5	8.1×10^6	2.5×10^5	-
		386	430	0.97	120.5	8.1×10^6	2.5×10^5	-
	Acetonitrile	256	429	0.93	154.7	6.0×10^6	4.5×10^5	-
		389	429	0.93	154.7	6.0×10^6	4.5×10^5	-
	Methanol	256	429	0.98	146.5	6.7×10^6	1.4×10^5	-
		389	429	0.98	146.5	6.7×10^6	1.4×10^5	-

* Φ_{i-c} : Quantum yield of *trans*→*cis* isomerization (Reference 19).
-: not measurable.

times is consistent with the increment of *trans*→*cis* photoisomerization quantum yield with increasing of solvent polarity, indicating that CT process is involved in a photoisomerization. This is consistent with the observation that the *trans*→*cis* photoisomerization quantum yield depends on excitation wavelength.¹⁹

In conclusion, we suggest that the first emission at 340 nm is originated from the S_2 state of the *cis*-form, and the S_1 state is the only singlet excited state producing a CT character to facilitate the photoisomerization. This suggestion is consistent with the result that the dual emission exhibit different excitation spectra. The emission observed from S_2 state depart from Kasha's rule that in condensed phases fluorescence is only observed from S_1 , phosphorescence is only observed from T_1 . The emission from S_2 has been observed for azulene,²² its derivatives,²³ aralkyl thiones,

thiophosgene etc. The reason for observation of $S_2 \rightarrow S_0$ fluorescence in azulene is the relatively large $S_2 \rightarrow S_1$ energy gap ($14,000 \text{ cm}^{-1}$) and slow $S_2 \rightarrow S_1$ internal conversion. Similarly, the $S_2 \rightarrow S_0$ fluorescence for I and II derivatives also have the relatively large $S_2 \rightarrow S_1$ energy gap ($14,000 \text{ cm}^{-1}$) as observed from the absorption spectra. Especially the fluorescence lifetime of the first emission becomes much longer for the *cis*-form than for the *trans*-form. This is consistent with the result that for I and II derivatives the *trans* \rightarrow *cis* photoisomerization takes place on direct irradiation while III and IV derivatives don't undergo photoisomerization. This is the reason why the first emission is originated from the S_2 state.

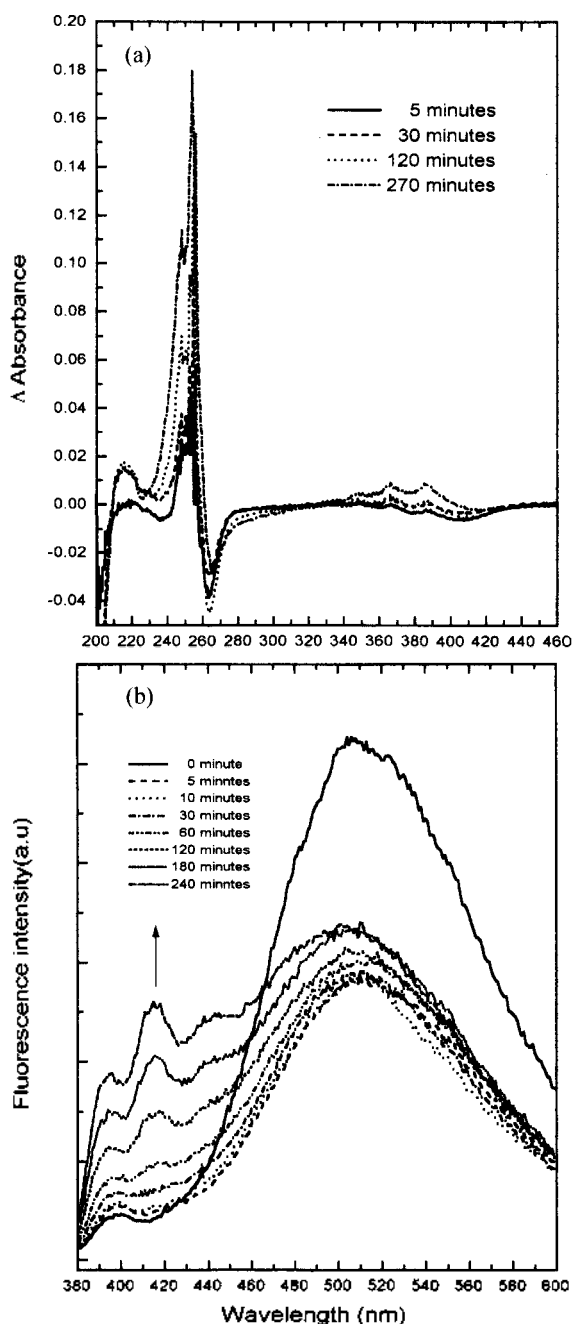
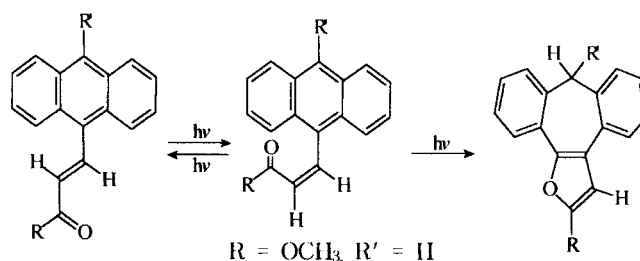


Figure 7. Absorption(a) and emission(b) spectra of *trans*-I in MeOH with various irradiation times.

In 1995 Gopal, Reddy, and Rao reported that for both I and II derivatives the *cis* \rightarrow *trans* photoisomerization was not observed on direct irradiation. In case of I, however, the change in absorption and fluorescence spectra is observed as shown in Figure 7. The absorption spectra show the isobestic point at 320 nm, implying that another species of I exists in equilibrium in the ground-state. Especially, there is dramatic change in the fluorescence behavior. The emission originated from the S_1 state is quenched with increasing irradiation time, followed by the appearance of new structured emission band around 430 nm. From absorption and fluorescence emission spectra of *cis*- and *trans*-I, the origin of the structured emission of 430 nm is clearly different from the S_1 or S_2 emission for *cis*- and *trans*-I. The irradiation-induced fluorescence changes are bigger in protic polar solvent than in nonpolar solvent as shown Figure 8, in which the relative intensity ratio of photo-induced emission to S_1 emission of *trans*-I in various solvents is plotted as a function of irradiation time. These results infer that the photo-induced emission is originated from a product formed by intramolecular $[4\pi+2\pi]$ cycloaddition reaction as already reported by Becker,^{15,24} Andersson,²⁴ etc. The intramolecular $[4\pi+2\pi]$ cycloaddition mechanism is briefly described at Scheme 2. Becker²⁵⁻²⁶ *et al.* reported that the intramolecular $[4\pi+2\pi]$ cycloaddition was rarely affected by molecular oxygen and geometrically facilitated when the distance between carbonyl oxygen and the reacting 9-position of anthracene presumably is not larger than 3 Å. In practice, the molecular structure of I



Scheme 2. Intramolecular $[4\pi+2\pi]$ cycloaddition mechanism of *trans*-I by photoirradiation.

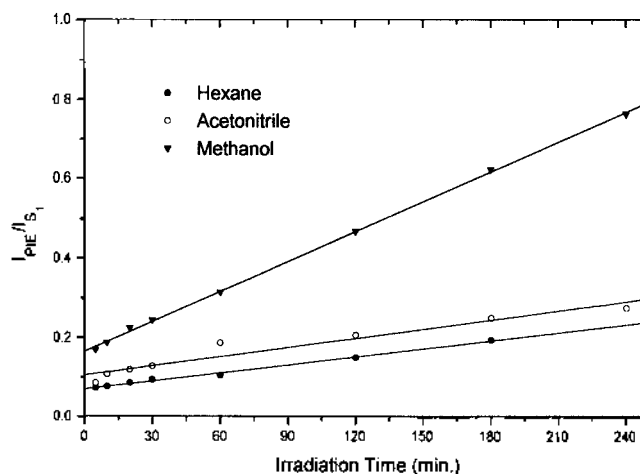


Figure 8. Relative intensity ratio of photo-induced emission to S_1 emission of *trans*-I in various solvents as a function of irradiation time.

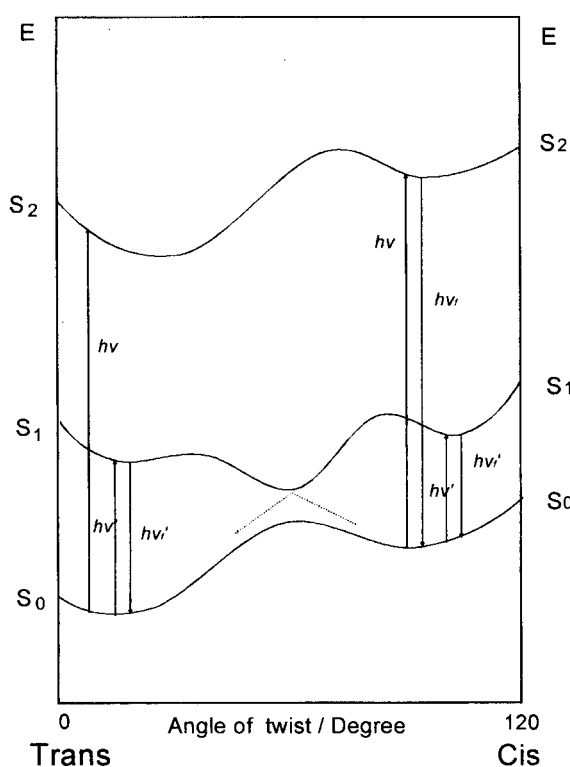


Figure 9. Proposed schematic representation of the ground -and excited- state potential surfaces for I & II.

derivative is very similar with molecular model suggested by Becker *et al.* The quantum yield of intramolecular $[4\pi+2\pi]$ cycloaddition reaction is increased as the polarity of solvent increases. This indicated that intramolecular $[4\pi+2\pi]$ cycloaddition reaction is more favorable for *cis* form than *trans* form.

Furthermore, Rao *et al.*¹⁹ reported that the photo-induced emission observed from I is assigned just as a locally excited state emission. They interpreted that the quenching of the locally excited state emission at high concentration was due to energy transfer process. For both pure I and II derivatives, however, the locally excited state emission is not observed in polar solvent as well as in nonpolar solvent. These results indicate that the locally excited state emission observed by Rao *et al.* is originated from photo-product formed in process of synthesis of 9-anthrylethylene derivatives. Thus, we can interpret that upon increasing of concentration of substrate, the quenching of locally excited state emission is not due to energy transfer for quantum chain isomerization but to self-absorption effect by high concentration of solute (1.5×10^{-3} – 6.0×10^{-3} M).

From above results, we suggest that the *cis*→*trans* isomerization does not take place because the formation of the S_1 state inducing a large CT character is restricted by the decrease of resonance contribution in excited state and the conjugation by the geometrical restraint of *cis* isomer that means the *cis*→*trans* isomerization is more favorable *via* triplet state than *via* S_1 state. In case of I derivative, especially, the *cis*→*trans* isomerization is largely hindered by the intramolecular $[4\pi+2\pi]$ cycloaddition. Furthermore, for I and II the emission of locally excited state proposed by Rao *et al.* are not observed in polar solvent as well as in

nonpolar solvent. Thus we could not observe the quenching of locally excited state emission with increasing of concentration of substrate. Therefore, we suggest that the 9-anthrylethylene derivatives (I and II) does not undergo isomerization *via* quantum chain process.

Conclusion

The photoisomerization and the fluorescence spectroscopic properties of 9-anthrylethylene derivatives have been measured in various solvents. From above results, it can be summarized that the photophysical processes and photoisomerization take place on the proposed potential energy surface as shown in Figure 9. The potential energy surface is consistent with the results which showed about 94% *trans*→*cis* isomerization for the S_0 → S_1 excitation and a low *trans*→*cis* isomerization for the S_0 → S_2 . We suggest that the first emission at 340 nm is originated from the S_2 state of the *cis*-form, and the S_1 state is the only singlet excited state inducing a large CT character to facilitate the photoisomerization. The formation of S_1 and S_2 state was found to depend markedly on the nature of the substituent on their ethylenic bonds and solvent polarity. The lifetime and quantum yield of fluorescence originated from S_1 for I and II is increased while those of S_2 is decreased with increasing of solvent polarity. For III and IV, however, no solvent dependence of the lifetime and quantum yield was observed. Especially, the second emission at 430 nm of I observed by Rao *et al.* is not originated from the locally excited state, but originated from a novel isomer formed by photoirradiation. These results indicate that the photoisomerization of 9-anthrylethylene derivatives I-II do not take place *via* quantum chain process.

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Intramolecular Hydrogen Bonding Effect on the Excited-State Intramolecular Charge Transfer of *p*-Aminosalicylic Acid

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The excited-state intramolecular proton transfer (ESIPT) emission has been observed for 0.01 mM *p*-aminosalicylic acid (AS) in nonpolar aprotic solvents as demonstrated by the large Stokes' shifted fluorescence emission around 440 nm in addition to the normal emission at 330 nm. However in aprotic polar solvent such as acetonitrile, the large Stokes' shifted emission band becomes broadened, indicating existence of another emission band originated from intramolecular charge transfer (ICT). It is noteworthy that in protic solvents such as methanol and ethanol the normal and ICT emissions are quenched as the AS concentration decreases, followed by the appearance of new emission at 380 nm. These results are interpreted in terms of ESIPT-coupled charge transfer in AS. Being consistent with these steady-state spectroscopic results, the picosecond time-resolved fluorescence study unravelled the decay dynamics of the ESIPT and ICT state *ca.* 300 ps and *ca.* 150 ps, respectively with *ca.* 40 ps for the relaxation time to form the ICT state.

Introduction

Aminosalicylate and its derivatives are well known molecules easily form the excited-state intramolecular proton transfer (ESIPT) through the intramolecular hydrogen bonding. For the first time, that was investigated by Kasha *et al.* several years ago. They suggested that some derivatives such as dialkylaminosalicylate form the triple fluorescence emission, normal locally excited-state emission, the proton transfer tautomer emission and the excited-state intramolecular charge transfer (ICT) emission which are in competitive with one another.^{1,2} Especially, the third emission, the excited-state ICT emission can be controlled by many other factors, as revealed by a lot of

reports for the excited-state ICT process which is a primary function for photoelectronic devices³ as well as a basic mechanism of biological and chemical energy conversion.⁴⁻⁷

As an example of that factor, in some molecules, such as dimethylaminobenzonitrile (DMABN) derivatives, the excited ICT state formation followed by the solvent relaxation is important in determining the overall charge-transfer process.⁸⁻¹² Some other authors proposed that the photoinduced charge separation can be maximized by coupling with a conformational change of the electron donor group such as the twist of the whole alkylamino group which leads to a so-called "twist intramolecular charge transfer (TICT)" state^{13,14} or the rehybridization of the nitrogen of the amino group, leads to the "wagged intramolecular charge transfer (WICT)" state.¹⁵ Besides, according to recent HF/SCF and CIS calculations, bending

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