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Photophysical properties and photoisomerization behaviour of 1-(9-anthryl)-2-(*n*-pyridyl)ethenes (*n* = 2, 3 or 4), aza analogues of 1-(9-anthryl)-2-phenylethene [1]

Eun Ju Shin [a,*], Eun Young Bae [a], Seung Hee Kim [a], Ho Kwon Kang [b], Sang Chul Shim [c]

[a] *Department of Chemistry, Sunchon National University, Sunchon, Chonnam 540-742, South Korea*

[b] *Department of Agricultural Chemistry, Sunchon National University, Sunchon, Chonnam 540-742, South Korea*

[c] *Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1, Kusong-dong, Yusong-Gu, Taejon 305-701, South Korea*

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Abstract

The quantum yields of fluorescence and photoisomerization of *trans*-1-(9-anthryl)-2-(*n*-pyridyl)ethenes (*n* = 2, 3 or 4) (t-*n*-APyE) and the corresponding cis isomers (*n* = 2 or 4) (c-*n*-APyE) were measured in various solvents. t-3-APyE is strongly fluorescent, but does not undergo photoisomerization, similar to *trans*-1-(9-anthryl)-2-phenylethene (t-9-APE). The fluorescence and photoisomerization of t-2-APyE and t-4-APyE are strongly influenced by the solvent polarity. In non-polar solvents, they show relatively strong fluorescence, but no photoisomerization to the corresponding cis isomers. As the solvent polarity is increased, the fluorescence intensity decreases and the photoisomerization to the cis isomer becomes efficient. An intramolecular charge transfer excited state is suggested to contribute to the photoisomerization. A singlet mechanism is proposed from the inverse relationship between the fluorescence and photoisomerization quantum yields over the range of solvent polarity and temperature used. A much weaker solvent effect was observed on the fluorescence and photoisomerization of c-2-APyE, and the fluorescence and photoisomerization of c-4-APyE were found to be independent of the solvent polarity. Efficient isomerization to the trans isomer was observed in both non-polar and polar solvents. © 1997 Elsevier Science S.A.

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1. Introduction

The photochemical cis–trans isomerization of stilbene and related 1,2-diarylethenes has been investigated extensively because of its importance in both theoretical and technological chemistry [1–7]. Stilbenes undergo geometrical trans ⇄ cis isomerization via an activated internal rotation in the excited singlet manifold on direct irradiation.

Recently, 1-(*n*-anthryl)-2-phenylethenes (*n*-APEs) (*n* = 1, 2 and 9) have attracted considerable attention because they belong to a family of 1,2-diarylethenes which exhibits one-way cis → trans adiabatic photoisomerization [8–20]. Considerable experimental and theoretical effort has been devoted to the photochemistry of *n*-APEs. The photoisomerization and photophysical behaviour of 2-APE and its derivatives have been studied extensively [8–11]. The ground state conformers arising from the rotation of the 2-anthryl group around the single bond linking it to the ethene make the problem very complicated. Arai and Tokumaru [8] have suggested that adiabatic cis → trans photoisomerization of 2-APE takes place in the triplet manifold. Recently, however, Saltiel et al. [9] and Mazzucato and coworkers [6] have proposed, independently, a singlet adiabatic photoisomerization pathway.

9-APE is a good candidate for the investigation of the one-way photoisomerization, because no distinct rotamers arise from a 180° rotation of the 9-anthryl group around the single bond [12]. It has been established for both cis (c-9-APE) and trans (t-9-APE) conformers that steric repulsions involving the vinyl group and H1/H8 of the anthracene preclude planar ground state conformations, so that the electronic conjugation of the styryl and anthracene systems is impaired even for the trans isomer [16]. c-9-APE [15] is photochemically converted into the trans isomer, but the reaction is irreversible, i.e. trans → cis isomerization is not observed. Interest-

Abbreviations: 9-APE, 1-(9-anthryl)-2-phenylethene; *n*-APyE, 1-(9-anthryl)-2-(*n*-pyridyl)ethene

* Corresponding author. Fax: +82 661 50 3608.

[1] In memory of Professor H.K. Kang, who died on December 2, 1995 at the age of 36 years.

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ingly, polar substituents in the para position of the styryl group have been found to facilitate the photochemical trans→cis isomerization of 9-APE, conceivably via intramolecular charge transfer processes [17,19]. As the medium polarity is increased, the photoisomerization of 9-APE derivatives bearing a polar substituent changes from a one-way to a two-way mode.

In this paper, we report the photophysical properties and photoisomerization behaviour of the aza analogues of 9-APE. 1-(9-Anthryl)-2-(*n*-pyridyl)ethenes (*n*-APyEs) (*n* = 2, 3 or 4) represent another example in which the photoisomerization is controlled by the environment. In contrast with parent 9-APE, trans→cis photoisomerization of *n*-APyEs is efficient in polar solvents and inefficient in non-polar solvents.

2. Experimental details

2.1. Synthesis

t-3-APyE was synthesized by the Wittig reaction of 9-anthrylmethyltriphenylphosphonium bromide (prepared by bromination of 9-methylanthracene using *N*-bromosuccinimide, followed by reaction with triphenylphosphine) and 3-pyridinecarboxaldehyde. t-2-APyE and t-4-APyE were prepared by the procedure reported in Refs. [21,22]. 1-Methyl-*n*-(2-(9-anthryl)vinyl)pyridinium iodides (*n* = 2 and 4) were prepared by heating a mixture of 9-anthraldehyde and 1,4-dimethylpyridinium iodide (prepared by the reaction of 4-picoline and excess iodomethane) with a piperidine catalyst in absolute ethanol, followed by refluxing with triphenylphosphine. The final products (t-*n*-APyEs) were chromatographed on a silica gel column using dichloromethane as eluent and recrystallized from a hexane–acetone mixture. c-2-APyE and c-4-APyE were prepared by irradiation of methanol solutions of t-2-APyE and t-4-APyE (1×10^{-3} M) at 350 nm for 2 h after degassing by bubbling with N_2 gas for 30 min. c-2-APyE and c-4-APyE were separated by silica gel column chromatography or preparative thin layer chromatography (TLC) using ethyl acetate–hexane (1 : 2, v/v) or hexane–dichloromethane–ethyl acetate (10 : 3 : 1, v/v) as eluent in a dark room because the cis isomers are very sensitive to light and revert rapidly to the trans isomers in daylight. c-3-APyE could not be prepared by irradiation of t-3-APyE. *n*-APyEs were characterized by NMR, IR, UV and mass spectral data.

2.2. Chemicals

For spectroscopic measurements and photochemical reactions, *n*-hexane, ethyl acetate, acetonitrile and methanol of high performance liquid chromatography (HPLC) grade (Merck) and methylcyclohexane (MCH) and ethanol of spectrophotometric grade (Aldrich) were used. Dichloromethane, toluene and tetrahydrofuran (THF) were freshly distilled from P_2O_5, CaH_2 and Na respectively. Quinine sulphate (Aldrich) was purified by recrystallization from water and used as a standard for fluorescence quantum yield measurements. Kiesel Gel 60 (70–230 mesh, Merck) and silica gel (TLC grade 7749, Aldrich) were used for silica gel column chromatography and TLC respectively.

2.3. Spectroscopic measurements

The absorption spectra were recorded on a Hitachi U-321097 spectrophotometer. An Aminco-Bowman Series 2 luminescence spectrometer was used for steady state fluorescence studies. For the determination of the fluorescence quantum yields, the absorbances of the solution at the excitation wavelength (360 nm) were kept below 0.1, usually at a value of 0.07–0.08, to avoid inner filter effects, and all the fluorescence spectra were corrected. The fluorescence quantum yields were determined by three independent measurements using quinine sulphate in 0.1 N H_2SO_4 ($\Phi_f = 0.55$ at the excitation wavelengths of 313 or 366 nm at 295 K) at room temperature and 9,10-diphenylanthracene in MCH ($\Phi_f = 1$) at 77 K as standards. The fluorescence spectra at 77 K were obtained by modification of the cell compartment using a Dewar assembly. The temperature dependence of the fluorescence was determined by cooling via a thermostatically controlled cell holder using a JEIO TECH RBC-11 refrigerated bath circulator. The fluorescence quantum yields at temperatures other than room temperature (as well as at 77 K) were evaluated using the assumption that the relative values of the absorbances and refractive indices are independent of the temperature. An SLM-Aminco 48000 S phase resolved spectrometer was used for measurements of the fluorescence lifetime.

2.4. Photolysis

Preparative photolyses were conducted at 350 nm with a Southern New England Rayonet Photochemical Reactor RPR 100 equipped with an RMA-500 Merry-Go-Round Unit and 16 RPR 3500 Å fluorescent lamps. Photoisomerization was carried out by irradiation of 1×10^{-3} M deoxygenated solutions and monitored by TLC.

Quantitative analyses of the photochemical trans–cis isomerization reaction were carried out by HPLC at a flow rate of 2 ml min^{-1} using methanol as eluent. HPLC was accomplished using a Merck LiChrosorb RP-18 or Waters μ-Bondapak C_{18} analytical column on a Spectra-Physics SP 8810-010 liquid chromatograph equipped with an SP8810 precision isocratic pump, a Spectra 100 variable wavelength detector and an SP4290 integrator.

The quantum yields of photoisomerization were determined using a home-built merry-go-round system equipped with a Hanovia 450 W medium-pressure Hg arc lamp. Corning glass filters (CS 0-52 and 7-60) were employed to isolate the wavelength of 366 nm and a solution filter (combination of 0.44% (w/v) $CuSO_4 \cdot 5H_2O$ in 2.7 M NH_4OH and 7.5% (w/v) $NaNO_2$ in H_2O) was used for the isolation of 438.5

nm light. Potassium ferrioxalate was used for chemical actinometry. A concentration of 1×10^{-3} M was employed, where the absorbance of the solution was above two and all the incident light was absorbed. Photolysis was carried out to below 5% conversion to avoid competition of the back and parallel reactions. The temperature dependence of the trans → cis photoisomerization was determined on irradiation for 30 min in an Aminco-Bowman Series 2 luminescence spectrometer by cooling via a thermostatically controlled cell holder using a JEIO TECH RBC-11 refrigerated bath circulator.

3. Results and discussion

3.1. Absorption and fluorescence spectra

The absorption spectra of t-*n*-APyEs ($n=2$, 3 and 4) (Fig. 1) and c-*n*-APyEs ($n=2$ and 4) (Fig. 2) appear in a similar region, but the cis isomers show a much weaker and more structured absorption than the corresponding trans isomers. The absorption spectra of t-*n*-APyEs are practically the same. Typically, for t-2-APyE, the absorption maximum (λ_a) is 387 nm ($\epsilon=16\,560$) with shoulders at 348 nm (7380) and 368 nm (13 330) in *n*-hexane. The λ_a values of c-2-APyE and c-4-APyE are also nearly identical. The λ_a values of c-2-APyE are 334 nm ($\epsilon=1760$), 351 nm (4020), 368 nm (6600) and 388 nm (6240) in *n*-hexane. All these compounds exhibit vibrational structure which characterizes the

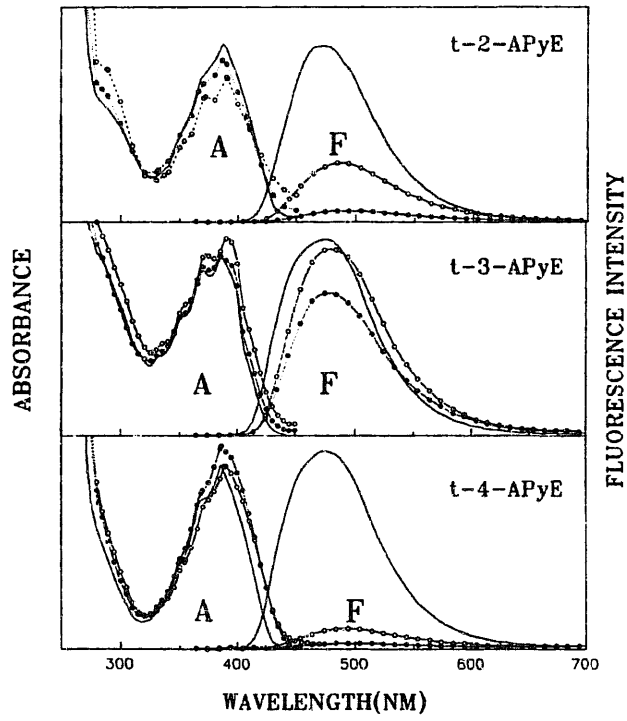

Fig. 1. Absorption (A) and corrected fluorescence (F) spectra of t-*n*-APyE ($n=2$, 3 and 4) in *n*-hexane (full line), dichloromethane (open circles) and methanol (filled circles) at room temperature (excitation wavelength, 360 nm).

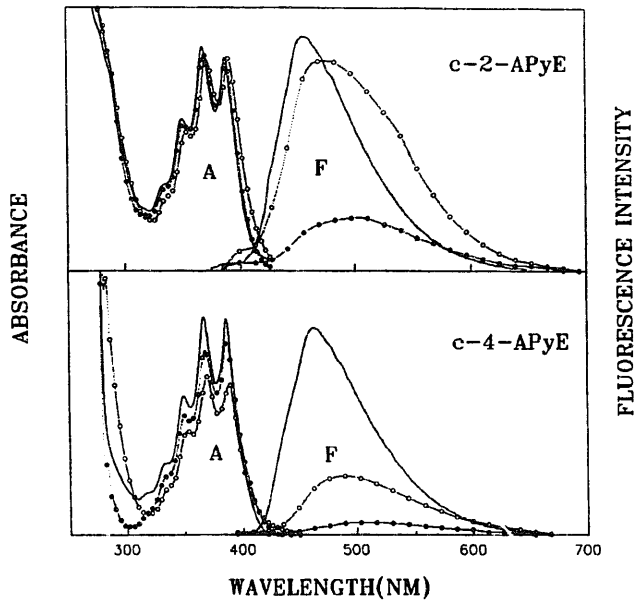

Fig. 2. Absorption (A) and corrected fluorescence (F) spectra of c-2-APyE (top) and c-4-APyE (bottom) in *n*-hexane (full line), dichloromethane (open circles) and methanol (filled circles) at room temperature (excitation wavelength, 360 nm).

absorption spectrum of the anthracene chromophore. The absorption spectra of all t-*n*-APyEs and c-*n*-APyEs remain nearly unchanged in solvents of various polarity. As in the parent 9-APE [12,15,17], the structured absorption spectra of the cis isomers can be distinguished from the broad spectra of the trans isomers. In the trans isomers, conjugation of the anthracene system with the vinylpyridine moiety leads to the partial loss of fine structure as in the case of t-9-APE. X-Ray diffraction analyses of crystalline c-9-APE and t-9-APE reveal that the angles between the plane of anthracene and the plane of the ethene double bond are 79° and 66° respectively [15]. The cis isomers have less conjugation between the anthracene ring and the vinylpyridine moiety, leading to a more twisted unstable structure than the trans isomers, and are easily isomerized on irradiation.

The fluorescence spectra of t-*n*-APyEs and c-*n*-APyEs at room temperature are shown in Figs. 1 and 2. Both cis and trans isomers show broad fluorescence spectra. As shown in Tables 1 and 2, the fluorescence maxima (λ_f) and quantum yields (Φ_f) of *n*-APyEs, except t-3-APyE, are strongly influenced by the solvent polarity, in contrast with Φ_f of parent t-9-APE which is independent of the solvent polarity [17]. As the solvent polarity is increased, λ_f is markedly red shifted and Φ_f is reduced. Therefore the Stokes shift ($\sigma_a-\sigma_f$) increases with increasing solvent polarity (Tables 1 and 2). This phenomenon is more pronounced for 4-APyE which has more polar charge transfer character. The marked Stokes shift represents the large difference between the ground and excited state geometry, as observed in parent 9-APE [12,17]. 9-Anthrylethene derivatives have a twisted geometry around the single bond linking the anthracene ring to the ethene in the ground state in order to reduce steric strain [6,12]. In the excited state, the order of this bond is increased and the

Table 1
Effect of solvent on the fluorescence maxima, quantum yields and lifetimes of fluorescence, quantum yields of photoisomerization and Stokes shifts for t-*n*-APyEs [a] ($n=2$, 3 and 4) and t-9-APE [b]

Solvent	$E_T(30)$ [c]	t-2-APyE					t-3-APyE [e]				t-4-APyE					t-9-APE				
		λ_f (nm)	τ_f (ns)	Φ_f	$\Phi_{t\rightarrow c}$	Stokes shift (cm^{-1})	λ_f (nm)	τ_f (ns)	Φ_f	Stokes shift (cm^{-1})	λ_f (nm)	τ_f (ns)	Φ_f	$\Phi_{t\rightarrow c}$	Stokes shift (cm^{-1})	λ_f (nm)	τ_f (ns)	Φ_f	$\Phi_{t\rightarrow c}$	Stokes shift (cm^{-1})
Hexane	30.9	473	3.5	0.49	– [d]	4698	475	3.7	0.43	4787	476	3.6	0.44	– [d]	4898	468 [f]	3.7	0.46 [f]	<0.01 [f]	–
Toluene	33.9	482	3.5	0.42	0.02	4763	475	4.0	0.33	4523	482	2.8	0.26	0.04	4894	478	3.6	0.45	<0.02	4731
THF	37.4	482	3.3	0.39	0.06	4960	483	4.1	0.45	4872	487	1.6	0.16	0.17	5107	474 [g]	3.7 [g]	0.42 [g]	–	–
EtOAc	38.1	481	2.9	0.36	0.07	4983	483	4.2	0.42	5136	483	1.4	0.15	0.27	5136	–	–	–	–	–
CH_2Cl_2	41.1	484	1.8	0.21	0.33	4901	480	4.1	0.40	4677	491	0.4	0.07	0.35	5407	478	3.6	0.40	–	–
CH_3CN	46.0	487	0.9	0.08	0.44	5173	480	3.6	0.38	4742	493	0.3	0.04	0.37	5623	476	4.2	0.45	0.003	–
EtOH	51.9	495	0.6	0.07	0.31	5571	480	3.3	0.38	4940	497	0.3	0.04	0.29	5800	474	3.9	0.44	<0.02	–
MeOH	55.5	495	–	0.05	0.38	5705	480	2.6	0.27	5006	501	–	0.04	0.27	5947	–	–	–	–	–

[a] At room temperature, excitation wavelength at 360 nm for steady state fluorescence and excitation wavelength at 385 nm and emission wavelength at 470 nm for fluorescence lifetime measurement; in argon-saturated solution at room temperature, irradiation wavelength of 366 nm for photoisomerization.
[b] Taken from Refs. [6,12,17].
[c] Dimroth's empirical solvent polarity parameter.
[d] Decomposition reaction is observed.
[e] For t-3-APyE, trans → cis photoisomerization is very inefficient.
[f] In cyclohexane.
[g] In MTHF.

Table 2
Effect of solvent on the emission maxima, quantum yields of fluorescence and photoisomerization and Stokes shifts for c-2-APyE, c-4-APyE [a] and c-9-APE [b]

Solvent	$E_T(30)$ [c]	c-2-APyE					c-4-APyE					c-9-APE			
		λ_f (nm)	Φ_f	$\Phi_{c\rightarrow t}$		Stokes shift (cm^{-1})	λ_f (nm)	Φ_f	$\Phi_{c\rightarrow t}$		Stokes shift (cm^{-1})	λ_f (nm)	Φ_f	$\Phi_{c\rightarrow t}$	Stokes shift (cm^{-1})
				0.0012 M	0.0003 M				0.0012 M	0.0003 M					
Hexane	30.9	468	0.14	– [e]	– [e]	4406	463	0.20	– [e]	– [e]	4175	460 [f]	0.16 [f]	0.22	–
Toluene	33.9	476	0.23	1.31	0.13	4502	477	0.06	0.80	0.27	4546	465	0.12	–	4401
THF	37.4	479	0.20	2.07	0.24	4764	480	0.03	0.59	0.26	4677	470 [d]	0.13	–	–
EtOAc	38.1	476	0.14	0.77	0.18	4699	471	0.02	0.68	0.22	4344	–	–	–	–
CH_2Cl_2	41.1	479	0.04	1.05	0.14	4699	488	0.009	0.33	0.22	5018	470	0.10	–	–
CH_3CN	46.0	487	0.02	1.36	0.19	5173	490	0.004	0.33	0.21	5233	469	0.04	0.41	–
EtOH	51.9	487	0.01	0.71	0.18	5173	497	0.006	0.35	0.20	5520	472	0.08	–	–
MeOH	55.5	487	0.01	1.18	0.16	5173	500	0.002	0.26	0.24	5641	–	–	–	–

[a] At room temperature, excitation wavelength at 360 nm for fluorescence, and in argon-saturated solution at room temperature, irradiation wavelength of 366 nm for photoisomerization.
[b] Taken from Refs. [6,17].
[c] Dimroth's empirical solvent polarity parameter.
[d] In MTHF.
[e] Decomposition reaction is observed.
[f] In cyclohexane.

anthracene nucleus tends to planarity with the ethene bond. The large Stokes shift can be understood in terms of excited state relaxation to a fluorescent state with an equilibrium geometry substantially displaced from the minimum in the ground state [12].

The fluorescence spectra of the trans isomers show very similar shapes to those of the corresponding cis isomers, except for a longer λ_f in the trans isomers. The λ_f value of t-4-APyE is shifted from 476 nm in *n*-hexane to 501 nm in methanol, and that of c-4-APyE is shifted from 463 nm in *n*-hexane to 500 nm in methanol. The energy of the first singlet excited state evaluated from the λ_a and λ_f data is similar for the three t-*n*-APyE isomers, but differs slightly in the order t-3-APyE > t-2-APyE > t-4-APyE.

As shown in Tables 1 and 2, all t-*n*-APyEs have Φ_f values in *n*-hexane similar to that of parent t-9-APE. However, as the solvent polarity is increased, the Φ_f values of t-2-APyE and t-4-APyE decrease, whereas that of t-3-APyE remains almost unchanged. The Φ_f value of 4-APyE is more rapidly reduced than that of the corresponding 2-isomer with increasing solvent polarity. The fluorescence quantum yields of the cis isomers are smaller than those of the trans isomers and c-4-APyE has a smaller fluorescence quantum yield than c-2-APyE.

The λ_f and Φ_f values of t-3-APyE are almost unaffected by the solvent polarity, because the lone pair electrons on the nitrogen atom at the meta position cannot effectively delocalize in the aromatic ring π system [3], and thus the excited state property seems to be similar to that of parent 9-APE. A similar example is found in styrylpyridines, as t-3-styrylpyridine (t-3-StPy) behaves differently from the other two isomers (t-2-StPy and t-4-StPy) [3,23].

3.2. Fluorescence lifetimes

The fluorescence lifetimes (τ_f) of t-*n*-APyEs in various solvents at room temperature are given in Table 1. The τ_f values of c-*n*-APyEs are too short to be measured with our instrument. All t-*n*-APyEs have τ_f values (3.5–3.7 ns) in *n*-hexane similar to that of parent t-9-APE (3.7 ns). As the polarity of the solvent increases, as with Φ_f, τ_f decreases for t-2-APyE and t-4-APyE, whereas τ_f is independent of the solvent polarity for t-3-APyE. As shown in Table 1, the τ_f values of t- and c-4-APyE are more rapidly reduced than those of the corresponding 2-isomers with increasing solvent polarity. The τ_f value of t-2-APyE is shortened to a few hundred picoseconds in acetonitrile, whereas τ_f of t-4-APyE is more rapidly decreased and reaches a few hundred picoseconds in dichloromethane. In very polar solvents, such as methanol, τ_f is too short to be measured. This also reflects the more polar character of t-4-APyE than t-2-APyE in the excited state.

From the data of Φ_f and τ_f, the fluorescence rate constants k_f of t-*n*-APyEs can be calculated using the equation $\Phi_f = k_f \times \tau_f$ and are reported in Table 4 (see Section 3.6). As the solvent polarity is increased, both the Φ_f and τ_f values decrease. The calculated k_f values for all t-*n*-APyEs are similar and independent of the solvent polarity. The decrease in Φ_f and τ_f in polar solvents may be due to an increase in efficiency of non-radiative processes including trans → cis photoisomerization. Unfortunately, there is no evidence to indicate whether different fluorescent states in non-polar and polar solvents are responsible for the decrease in Φ_f and τ_f in polar solvents.

3.3. Effect of concentration on fluorescence

t-2-APyE and t-4-APyE show broad fluorescence spectra in non-polar solvents. As the solvent polarity is increased, anthracene-like structured peaks at shorter wavelengths become intense. No significant difference is observed between the fluorescence excitation spectra taken at short fluorescence wavelength and long fluorescence wavelength. Therefore the structured emission at short wavelength is not due to an impurity. The effect of concentration on the fluorescence spectra of t-*n*-APyEs in *n*-hexane, dichloromethane and methanol was examined. For t-4-APyE in methanol, which shows the most pronounced dual emission, the short-wavelength structured emission is reduced with increasing concentration due to self-quenching (Fig. 3). A similar dual emission phenomenon has been observed in some 9-anthrylethene derivatives containing electron-withdrawing substituents [20]. The large Stokes shift of the longer wavelength fluorescence band for t-4-APyE in polar solvents reveals the intramolecular charge transfer character in the excited state. It is inferred that the longer wavelength band is due to a charge transfer state and the shorter wavelength structured band is due to a locally excited state. t-4-APyE also exhibits dual emission in the moderately polar solvent dichloromethane. The dual emission phenomenon is very weak for

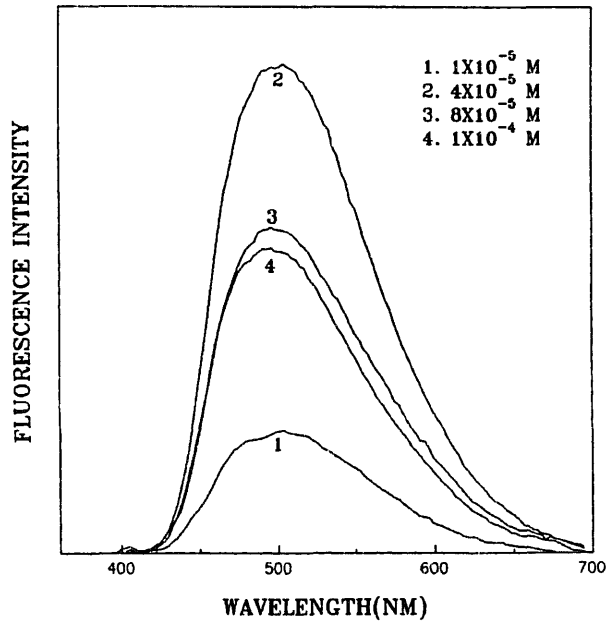

Fig. 3. Fluorescence emission of t-4-APyE at various concentrations in methanol at room temperature (excitation wavelength, 360 nm).

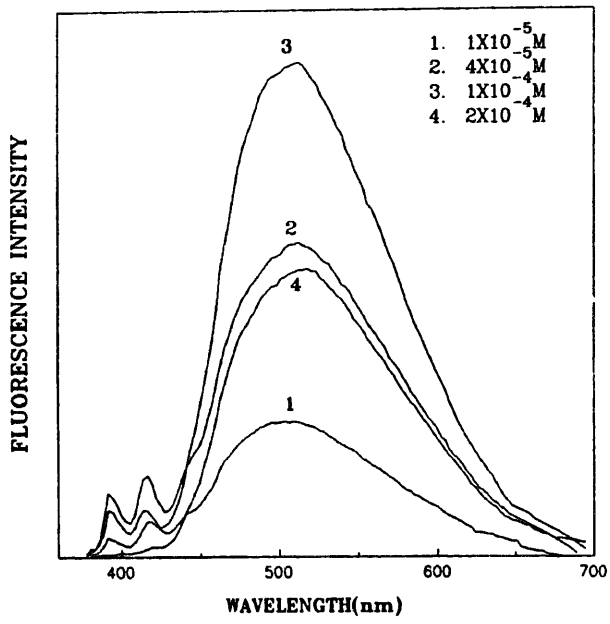

Fig. 4. Fluorescence emission of t-2-APyE at various concentrations in methanol at room temperature (excitation wavelength, 360 nm).

t-2-APyE even in methanol (Fig. 4) and cannot be observed for t-3-APyE in the solvents used.

3.4. Effect of excitation wavelength on the fluorescence

On varying the excitation wavelength between 300 and 400 nm at room temperature, no noticeable change is observed in the fluorescence spectra of t-*n*-APyEs in *n*-hexane, THF and methanol, indicating that t-*n*-APyEs exhibit no rotational isomerism at room temperature similar to parent 9-APE [12]. Even at 77 K, the fluorescence maxima do not change greatly with varying excitation wavelength.

3.5. Fluorescence at 77 K

For the trans isomers, the fluorescence becomes structured and blue shifted on going from room temperature to 77 K, and the fluorescence maxima are almost independent of the solvent polarity at 77 K when tested in MCH, 2-methyltetrahydrofuran (MTHF) and ethanol (Fig. 5 and Table 3), showing a similar trend to parent t-9-APE. t-9-APE in MTHF at room temperature exhibits λ_f at 474 nm, but at 77 K the fluorescence is characterized by maxima at 439 and 462 nm [22]. For t-4-APyE, λ_f at room temperature is 476 nm in *n*-hexane, but fluorescence at 77 K shows two maxima at 437 and 458 nm in cyclohexane. The fluorescence spectra of the cis isomers at 77 K are still broad, but blue shifted from those at room temperature (Fig. 6 and Table 3). The λ_f value of c-2-APyE around 430 nm is almost independent of the solvent polarity, but that of c-4-APyE is red shifted with increasing solvent polarity from MCH (449 nm) to ethanol (462 nm) at 77 K.

The Φ_f values of the trans isomers at 77 K are relatively high. In the determination of Φ_f at 77 K, significant error may be included because it is assumed that the absorbance ratio of the sample (*n*-APyE) and reference (9,10-diphenylanthracene) does not change on going from room temperature to 77 K. For t-3-APyE, Φ_f at 77 K is near unity in ethanol. Φ_f of t-4-APyE at 77 K is unity in MCH, but small (0.26) in MTHF, in which another UV absorption band is observed probably due to decomposition. At 77 K, the Φ_f values of the cis isomers are smaller than those of the corresponding trans isomers, and c-4-APyE has a lower fluorescence quantum yield than c-2-APyE, as observed at room temperature.

3.6. Quantum yields of photoisomerization

The quantum yields of direct trans→cis photoisomerization ($\Phi_{t\rightarrow c}$) of t-2-APyE and t-4-APyE at 366 nm are strongly dependent on the solvent polarity (Table 1). For example, t-*n*-APyEs undergo very inefficient trans→cis photoisomerization in non-polar solvents, similar to parent 9-APE [12,15,17], whereas $\Phi_{t\rightarrow c}$ for t-2-APyE and t-4-APyE increases as the solvent polarity increases. $\Phi_{t\rightarrow c}$ is virtually zero for t-3-APyE even in polar solvents. t-3-APyE exhibits considerable Φ_f in solvents of various polarity and no photoisomerization is observed in any of the solvents tested. Other reactions or decomposition are observed on prolonged irradiation. $\Phi_{t\rightarrow c}$ and Φ_f of t-2-APyE and t-4-APyE show, at least partly, an inverse relationship with varying solvent polarity (Table 1). As the solvent polarity increases, Φ_f decreases and $\Phi_{t\rightarrow c}$ increases. It is inferred tentatively that the photoisomerization of t-2-APyE and t-4-APyE proceeds on the excited singlet surface as in parent 9-APE and its derivatives [6,17,19,20]. It is probable that polar solvents stabilize the charge transfer state relative to the locally excited

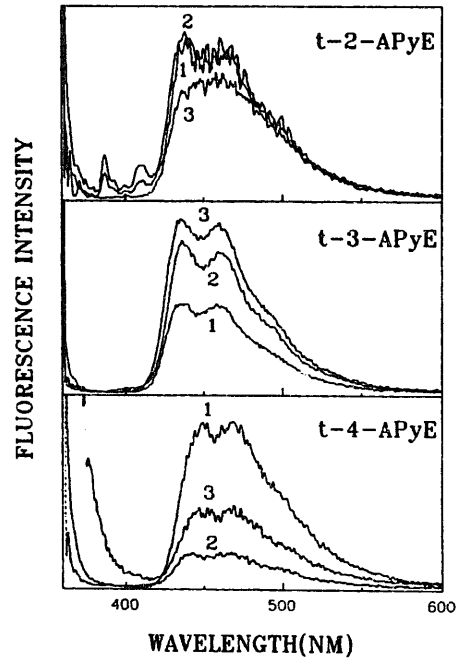

Fig. 5. Corrected fluorescence spectra of t-2-APyE (top), t-3-APyE (middle) and t-4-APyE (bottom) in MCH (1), MTHF (2) and ethanol (3) at 77 K (excitation wavelength, 360 nm).

Table 3
Maxima and quantum yields of fluorescence for *n*-APyE ($n=2$, 3 and 4) [a] and 9-APE [b] at 77 K

Solvent	$E_T(30)$[c]	t-2-APyE		t-3-APyE		t-4-APyE		t-9-APE		c-2-AVP		c-4-AVP		c-9-APE	
		λ_f (nm)	Φ_f	λ_f (nm)	Φ_f	λ_f (nm)	Φ_f	λ_f (nm)	Φ_f	λ_f (nm)	Φ_f	λ_f (nm)	Φ_f	λ_f (nm)	Φ_f
MCH	31.2	438, 465	0.55	436, 459	0.67	447, 468	1.03	438, 460[d]	0.48[d]	427	0.51	445	0.34	440[d]	0.60[d]
MTHF	36.5	438, 462	0.59	436, 460	0.93	442, 466	0.25	439, 462	0.50	427, 447	0.59	449	0.20	440	0.60
EtOH	51.9	462	0.51	436, 460	1.02	447, 468	0.39	434, 460	0.56	427, 448	0.28	460	0.16	442	0.60

[a] At 77 K, excitation wavelength at 360 nm using 9,10-diphenylanthracene in methylcyclohexane ($\Phi_f=1.0$) as a reference. In the determination of Φ_f at 77 K, significant error may be included because it is assumed that the absorbance ratio of the sample (*n*-APyE) and reference (9,10-diphenylanthracene) does not change on going from room temperature to 77 K.
[b] Taken from Ref. [17].
[c] Dimroth's empirical solvent polarity parameter.
[d] In 2,2-dimethylbutane–*n*-pentane (8 : 3, v/v).

state and shift the equilibrium in the excited trans isomer towards the charge transfer state, opening a pathway of trans → cis photoisomerization. The excited state involved in trans → cis photoisomerization is presumed to be a polar intramolecular charge transfer excited state, as in certain 9-APE derivatives containing electron-donating [19] and electron-accepting [17] substituents on the para position of the phenyl moiety and in certain 9-anthrylethene derivatives containing electron-withdrawing substituents such as ester or nitrile [20]. The introduction of a nitrogen atom into the phenyl moiety of 9-APE must enhance the polarity of the excited state and thereby $\Phi_{t\rightarrow c}$. $\Phi_{t\rightarrow c}$ of t-4-APyE is enhanced more than that of t-2-APyE as the solvent polarity increases, reflecting the more polar character of t-4-APyE compared with t-2-APyE. The error due to the very rapid cis → trans photoisomerization of the initially formed cis isomer in the measurement of $\Phi_{t\rightarrow c}$ cannot be excluded. This may be the reason

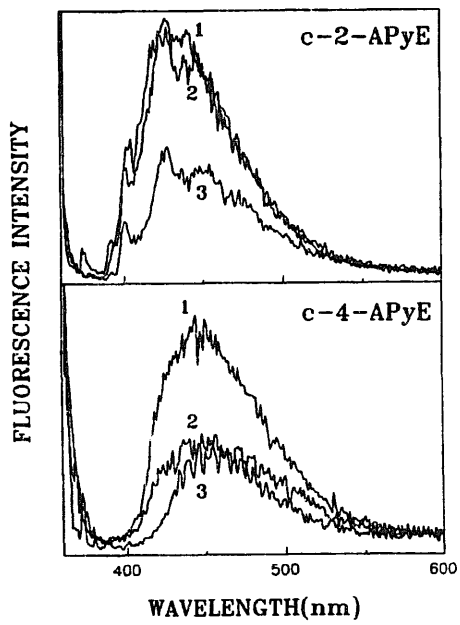

Fig. 6. Corrected fluorescence spectra of c-2-APyE (top) and c-4-APyE (bottom) in MCH (1), MTHF (2) and ethanol (3) at 77 K (excitation wavelength, 360 nm).

why t-4-APyE exhibits a slightly lower $\Phi_{t\rightarrow c}$ value than t-2-APyE in very polar solvents such as methanol. c-4-APyE, formed during the photoisomerization of t-4-APyE, undergoes very fast cis → trans photoisomerization. As a result, the apparent $\Phi_{t\rightarrow c}$ is smaller than that expected in methanol.

Because the sum of the fluorescence and photoisomerization quantum yields does not account for all the absorbed quanta, other competitive relaxation processes, such as intersystem crossing to the triplet state, may play a significant role in the deactivation of t-*n*-APyEs. If the trans → cis photoisomerization of t-*n*-APyEs contains contributions from a diabatic process (via internal conversion at the excited perpendicular configuration), as in the photoisomerization of stilbenes, the overall non-radiative deactivation efficiency except photoisomerization, i.e. the sum of the internal conversion and intersystem crossing quantum yields, is given by $\Phi_{NR}=1-\Phi_f-2\Phi_{t\rightarrow c}$ (Table 4). The partitioning factor from the ground perpendicular configuration to the trans and cis isomers is assumed to be 0.5. Φ_{NR} of t-*n*-APyEs is relatively high in non-polar solvents, implying efficient intersystem crossing. In parent 9-APE (triplet formation yield of 0.40 in cyclohexane) and its derivatives, a substantial yield of triplet formation has been reported [17,25]. The Φ_{NR} values of t-2-APyE and t-4-APyE are dependent on the solvent polarity, whereas that of t-3-APyE remains almost unchanged in various solvents. It is probable that the triplet formation yields of t-2-APyE and t-4-APyE may be dependent on the solvent polarity, similar to t-9-APE derivatives containing polar substituents [17,25].

The $\Phi_{c\rightarrow t}$ values of c-2-APyE and c-4-APyE (Table 2) are relatively high in all the solvents tested, whereas the $\Phi_{t\rightarrow c}$ values of the trans isomers are very low in non-polar solvents and increase with increasing solvent polarity. Therefore the trans isomer is rich at the photostationary state in non-polar solvents but, in polar solvents, both $\Phi_{t\rightarrow c}$ and $\Phi_{c\rightarrow t}$ are high. In *n*-hexane, the $\Phi_{c\rightarrow t}$ values of c-2-APyE and c-4-APyE are very low due to competition with the photocyclization or decomposition pathway. For the reference compound (c-9-APE), the photocyclization reaction has recently been

Table 4
Fluorescence rate constants (k_f) [a] and the overall non-radiative deactivation quantum yield except photoisomerization (Φ_{NR}) [b] of t-*n*-APyEs ($n=2, 3$ and 4) in various solvents at room temperature

Solvent	$E_T(30)$ [c]	t-2-APyE		t-3-APyE		t-4-APyE		t-9-APE	
		$k_f\times10^{-9}$ (s^{-1})	Φ_{NR}	$k_f\times10^{-9}$ (s^{-1})	Φ_{NR}	$k_f\times10^{-9}$ (s^{-1})	Φ_{NR}	$k_f\times10^{-9}$ (s^{-1})	Φ_{NR}
Hexane	30.9	0.14	0.51	0.12	0.57	0.12	0.56	0.12	0.52–0.54
Toluene	33.9	0.12	0.54	0.08	0.67	0.09	0.66	0.13	0.51–0.55
THF	37.4	0.12	0.49	0.11	0.55	0.10	0.50	0.11	0.58
EtOAc	38.1	0.12	0.50	0.10	0.58	0.11	0.31	–	–
CH_2Cl_2	41.1	0.12	0.13	0.10	0.60	0.18	0.23	0.11	0.60
CH_3CN	46.0	0.09	0.04	0.11	0.62	0.13	0.22	0.11	0.54–0.55
EtOH	51.9	0.12	0.31	0.12	0.62	0.13	0.38	0.11	0.52–0.56
MeOH	55.5	–	0.19	0.10	0.73	–	0.42	–	–

[a] Fluorescence rate constants k_f were calculated by the relationship $k_f=\Phi_f/\tau_f$ using the values in Table 1.
[b] The overall non-radiative deactivation quantum yield except photoisomerization (Φ_{NR}) is roughly calculated by $\Phi_{NR}=1-\Phi_f-2\Phi_{t\rightarrow c}$, and equivalent to the sum of internal conversion and intersystem crossing quantum yields, i.e. $\Phi_{NR}=\Phi_{ic}+\Phi_{isc}$. The partitioning factor α from the perpendicular configuration to trans and cis isomers is assumed to be 0.5.
[c] Dimroth's empirical solvent polarity parameter.

described [24]. $\Phi_{c\rightarrow t}$ increases with concentration and exceeds unity for c-2-APyE at a concentration of 1.2×10^{-3} M, which is attributable to "quantum chain" photoisomerization [8,20]. c-4-APyE has a higher $\Phi_{c\rightarrow t}$ value than c-2-APyE at a concentration of 3×10^{-4} M. The more polar nature of c-4-APyE relative to c-2-APyE should lead to more efficient photoisomerization. However, at a concentration of 1.2×10^{-3} M, the $\Phi_{c\rightarrow t}$ value of c-2-APyE is higher than that of c-4-APyE; no noticeable dependence of $\Phi_{c\rightarrow t}$ on the solvent polarity is observed for c-2-APyE, but $\Phi_{c\rightarrow t}$ of c-4-APyE decreases as the solvent polarity increases. This shows that, in non-polar solvents, one-way cis→trans photoisomerization proceeds but, in polar solvents, trans→cis as well as cis→trans photoisomerizations are efficient; thus t-4-APyE, initially formed by isomerization of c-4-APyE, reverts rapidly to the cis isomer and/or another decay pathway becomes efficient in polar solvents. The barrier against twisting in the excited state is expected to be higher for t-2-APyE than for t-4-APyE; excited t-2-APyE, formed by twisting of c-2-APyE, is deactivated rapidly, competing with isomerization and transfer of excitation energy to c-2-APyE, thereby propagating quanta leading to a $\Phi_{c\rightarrow t}$ value greater than unity. However, excited t-4-APyE, formed on irradiation of c-4-APyE, fluoresces in competition with isomerization, because the barrier against twisting is sufficiently low to compete with fluorescence. As a result, $\Phi_{c\rightarrow t}$ is higher for c-2-APyE than for c-4-APyE at higher concentration.

In stilbene [1], excitation leads the trans isomer to a perpendicular state in which the central double bond is twisted by 90°. The excited perpendicular state which is at a minimum on the lowest excited singlet potential energy surface undergoes internal conversion to the ground perpendicular state from which both trans and cis ground state isomers are produced (diabatic process). In 9-APE, most of the excitation energy is delocalized on the anthracene ring [6,8]. Thus the relative energy of the excited perpendicular state is no longer at a minimum. Two mechanisms have been proposed to explain the one-way photoisomerization of 9-APE and other diarylethenes [6,8]. One mechanism involves a diabatic process [19]. The energy minimum on the excited singlet potential energy surface shifts slightly from a 90° twisted perpendicular conformation to a transoid conformation. Deactivation from this energy minimum, attainable by excitation of the cis or trans isomer to the ground state energy surface, gives only the trans isomer. Alternatively, the excited perpendicular state is not at a minimum, but at a maximum, and excitation of the cis isomer generates the excited trans isomer directly by twisting the central ethene bond by 180°, overcoming an energy barrier across the excited perpendicular conformation from the excited cis conformation. The excited trans isomer is deactivated to the ground state trans isomer (adiabatic process) [6]. However, on excitation of the trans isomer, the barrier against twisting is too high for isomerization to occur. The latter adiabatic mechanism is more generally accepted because the quantum chain process can be explained [6,8].

Parent 9-APE exhibits no trans→cis photoisomerization due to the high activation barrier on the excited singlet potential energy surface, but only cis→trans isomerization [6,16,17]. Replacement of the phenyl ring in 9-APE by pyridine should induce some change on the excited singlet potential energy surface such that the activation barrier against twisting and/or the energy of the excited perpendicular state will be lowered via an intramolecular charge transfer process. As a result, 2-APyE and 4-APyE give rise to trans→cis photoisomerization, at least in polar solvents. In polar solvents, trans→cis photoisomerization becomes feasible through intramolecular charge transfer, thereby lowering Φ_f and shortening τ_f. This trend is more pronounced in t-4-AVP.

Azulene quenching experiments on photoisomerization were carried out using azulene concentrations in the range 1×10^{-3}–8×10^{-3} M. The Stern–Volmer quenching constants are very small for t-2-APyE and t-4-APyE as shown in Fig. 7. No corresponding cis isomers are observed in the

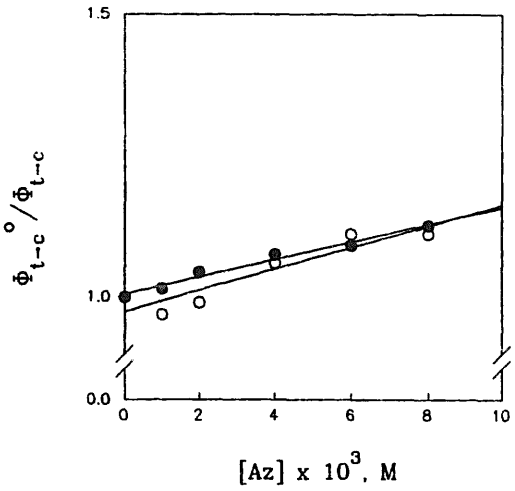

Fig. 7. Stern–Volmer plots for photoisomerization of t-2-APyE (filled circles) and t-4-APyE (open circles) in toluene at an irradiation wavelength of 366 nm.

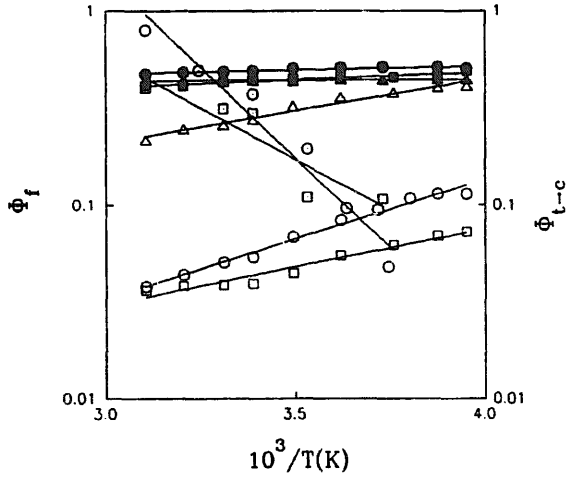

Fig. 8. Temperature dependence of log Φ_f in hexane (filled symbols) and methanol (open symbols) and log $\Phi_{t\to c}$ in methanol (open dotted symbols) for t-2-APyE (circles), t-3-APyE (triangles) and t-4-APyE (squares).

biacetyl-sensitized photoisomerization of t-2-APyE and t-4-APyE on irradiation at 435.8 nm. These results support the singlet mechanism for photoisomerization as suggested above.

3.7. Effect of temperature on Φ_f and $\Phi_{t\to c}$

The temperature dependence of Φ_f and $\Phi_{t\to c}$ in *n*-hexane and methanol between 25 and −20 °C is summarized in Fig. 8 for t-*n*-APyEs. The Φ_f values of t-2-APyE and t-4-APyE in polar solvents are smaller than those in non-polar solvents at room temperature, but the Φ_f values at 77 K are high and similar in solvents of different polarity. It is expected that, in polar solvents, as the temperature is lowered, Φ_f will increase and $\Phi_{t\to c}$ will decrease. In *n*-hexane, Φ_f and $\Phi_{t\to c}$ of t-*n*-APyEs are nearly independent of temperature. However, for t-2-APyE and t-4-APyE in methanol, $\Phi_{t\to c}$ is decreased and Φ_f is increased with decreasing temperature. For t-2-APyE, steeper slopes in the plots of $\Phi_{t\to c}$ and Φ_f vs. T^{-1} are observed than for t-4-APyE, indicating a higher activation barrier to isomerization for t-2-APyE, although no Arrhenius-type analysis was conducted. The Φ_f values of t-3-APyE (high at room temperature as well as at 77 K independent of the solvent polarity) are unaffected by the temperature even in methanol.

Because no temperature dependence of Φ_f for t-3-APyE is observed in the temperature range between 25 and −20 °C, the activation barrier to twisting in the first excited singlet state of t-3-APyE is thought to be more than 50 kJ mol^{-1}, similar to 9-APE [6]. Accordingly, the barrier to isomerization in the excited singlet manifold decreases in the order t-3-APyE > t-2-APyE > t-4-APyE, probably due to the increase in intramolecular charge transfer character. Both solvent and temperature effects imply that trans → cis photoisomerization and fluorescence of these compounds proceed via a common excited state, i.e. the excited singlet state.

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