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Photochemical Cis–Trans Isomerization of 5-Styryl-1,3-dimethyluracil

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The cis–trans photoisomerization of 5-styryl-1,3-dimethyluracil is investigated. The fluorescence and photoisomerization quantum yields in various solvents of different viscosity and polarity, the effect of salt, pH, and heavy atom on the fluorescence and photoisomerization, the triplet sensitization of the photoisomerization, and the azulene quenching of the direct and sensitized isomerization indicate the singlet mechanism for the direct photoisomerization of the compound. The laser flash photolysis at room temperature showed a weak triplet-triplet absorption indicating some intersystem crossing from the excited singlet state to the triplet state.

The photochemical cis–trans isomerization of olefinic compounds has been extensively studied and is one of the best-known photoreactions.[1–4] Nonetheless, its mechanistic details have been the subject of much controversy.

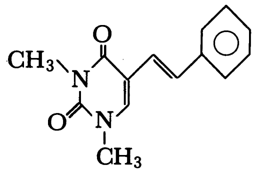
From the theoretical calculations and spectroscopic observations for stilbene, it was proposed that the activated internal rotation about the central double bond in the excited ^{1}S state should be followed by internal conversion of ^{1}S to ^{2}S with a minimum energy for the twisted geometry leading to $^2\mathrm{S}\rightarrow{}^0\mathrm{S}$ internal conversion thereby isomerizing.[5–7]

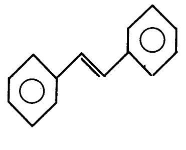
The photochemical and photophysical properties of heteroaromatic compounds has been given much attention because the (n,π^*) states introduced by the heteroatom affect the photochemical behavior. The proximity of (n,π^*) states to the lowest (π,π^*) states increases radiationless transitions to deactivate the excited molecules. Azastilbenes, typical examples of olefins with heteroaromatic moiety, have attracted some interests.[8–11] With photoisomerization, a variety of reactions including photochemical addition, reduction, substitution, and elimination processes have been observed which evidently originate via hydrogen atom abstraction by an electron-deficient nitrogen.[12,13] The styrylpyridines (StP's) and 1,2-dipyridylethylenes (DPE's) have very low fluorescence and photoisomerization quantum yields when the heteroatom is in the ortho or para position[9,10] due to the fast deactivation of the excited singlet state through efficient internal conversion. The singlet mechanism has been proposed for the direct photoisomerization of StP's and DPE's.[9,10]

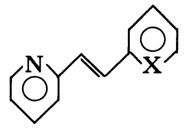
Pyrimidine nucleosides substituted at the C-5 position constitute a class of biologically significant molecules[14,15] and it is interesting to study the photochemical behavior of these molecules. We report here the cis–trans photoisomerization of (*E*)-5-styryl-1,3-dimethyluracil (5(*E*)-SDU) as a model for C-5 modified pyrimidine bases.

Experimental

Materials. (*E*)-5-Styryl-1,3-dimethyluracil (5(*E*)-SDU) was prepared by palladium-catalyzed reaction[16,17] of styrene and 1,3-dimethyluracil.[18] The reaction mixture was resolved on a silica-gel column using ethyl acetate–cyclohexane–chloroform (1/1/2, v/v) as the eluent, and recrystallized from 1-octanol: Mp 145.5—147.5 °C; Mass spectrum *m/z* 242 (molecular ion) 157 $(\mathrm{M^+{-}C_3ON_2H_5})$ 115 $(\mathrm{M^+{-}C_5O_2N_2H_7})$; UV $(\mathrm{CHCl_3})$ $\lambda_{\max}$ 316 nm (ε 24500); ^{1}H NMR $(\mathrm{CDCl_3})$ δ=7.25 (m, 5H, aromatic), 7.4 (d, 1H, phCH=), 6.8 (d, 1H, U-CH=), 3.53, 3.5 (s, 3H, N-$\mathrm{CH_3}$). 5(*E*)-SDU in acetonitrile was irradiated with benzophenone as a sensitizer at 350 nm in a Rayonet photochemical reactor for 2 h after the solution was degassed by bubbling with $\mathrm{N_2}$ gas for 1 h. 5(*Z*)-SDU was separated by column chromatography over silica gel and recrystallized from ethanol: UV $(\mathrm{CHCl_3})$ $\lambda_{\max}$ 255, 305 nm (ε 5000); ^{1}H NMR $(\mathrm{CDCl_3})$ δ=7.25 (m, 5H, aromatic), 7.3 (d, 1H, phCH=), 6.5 (d, 1H, U-CH=), 3.4, 3.2 (s, 3H, N-$\mathrm{CH_3}$).


5(E)-SDU


STILBENE


X = C, 2-StP
X = N, 2,2′-DPE

Benzophenone (Sigma) was recrystallized from cyclohexane. Azulene (Aldrich) was purified by vacuum sublimination. Commercially available styrene, uracil, mercury(II) acetate, trimethyl phosphate (Aldrich), and palladium chloride (Inuisho) were used without further purification. Extra pure solvents were used as received or after purification by distillation or standard methods.[19,20]

Spectra. NMR spectra were measured on a Varian T-60A spectrometer. Mass spectra were determined with a Hewlett Packard 5985 A GC/MS system by electron impact method. UV spectra were recorded on a Cary 17 spectrophotometer. Fluorescence spectra were recorded on an Aminco Bowman spectrofluorometer. Fluorescence quantum yields were determined using quinine hydrogen sulfate (Φ_f=0.546) as a reference. The fluorescence lifetime was measured at room temperature with SLM Model 480 phase modulation spectro-

Table 1. Phtoisomerization and Fluorescence Quantum Yields, Fluorescence Lifetimes, and Rotation Barriers of 5(*E*)-SDU and Other Stilbene Derivatives[9,10,24]

Compound	Φ_f	$\Phi_{t\text{-}c}$	τ_f/ns	ΔE_f/kcal mol^{-1}
5(*E*)-SDU	0.023[a]	0.048[b]	0.042	3.0[c]
Stilbene	0.036	0.41	0.09	3.2
2-Stp	0.0008	0.25	0.007	2.0
3-StP	0.075	0.56	0.19	3.3
4-StP	0.0016	0.37	0.008	0.8
2,2′-DPE	0.005	0.01		
3,3′-DPE	0.13	0.08		
4,4′-DPE	0.0004	0.003		

a) In ethanol. b) In benzene. c) In methylcyclohexane–isopentane (1:1, v/v).

photofluorometer.

Quantum Yields of Isomerization. Three ml samples in Pyrex ampoules were degassed by freeze-pump-thaw method and then sealed. These samples were irradiated in a merry-go-round apparatus with Hanovia 450 W medium-pressure mercury arc lamp (Type 697A36). Corning glass filters CS 0-52 and 7-37 were used to isolate 366 nm UV light. Light intensities were measured by trioxalatoferrate(III) actinometry.[21] Samples were analyzed by HPLC on a Waters Associates Model 244 liquid chromatograph. Reactions were carried out to less than 5% conversion to avoid competition with the back reaction.

Laser Flash Photolysis. The nanosecond laser photolysis apparatus has been described elsewhere.[22] A XeF (351 nm) and a KrF (248 nm) excimer laser (Lambda Physik EMG101E) were used as excitation light sources. The concentrations (1.5×10^{-5}—5.9×10^{-5} M^{-1}) of 5(*E*)- and 5(*Z*)-SDU were adjusted such that suitable amount of the laser light was absorbed. The lifetime for decay of the transient of 5(*E*)-SDU was obtained from oscillograms.

Results and Discussion

Fluorescence Studies. The fluorescence quantum yield and lifetime of 5(*E*)-SDU are lower and shorter than those of stilbene and meta-isomers of StP's and DPE's, but higher and longer than those of ortho- and para-isomers of StP's and DPE's (Table 1). The lone-pair electrons of N-atoms are conjugated with olefinic π-electrons more easily in ortho- and para-positions than in meta-position, so that the $^1(n,\pi^*)$ electronic configuration, inducing the nonradiative process, is involved to more extent in the former positions than in the latter one. The results suggest that the lone-pair electrons of N-atoms in 5(*E*)-SDU is not sufficiently delocalized as in 3-StP[10,23] and 3,3′-DPE and give less contribution to radiationless transition than in 2- and 4-StP's and 2,2′- and 4,4′-DPE's. The fluorescence quantum yield is strongly enhanced at liquid nitrogen temperature and the laser flash photolysis experiments show low Φ_{isc} for 5(*E*)-SDU at room temperature. Therefore, the deactivation of 5(*E*)-SDU at room temperature is mainly attributable to internal conversion rather than to intersystem crossing.

Table 2. Quantum Yields of Fluorescence and Direct Photoisomerization of 5-SDU in Various Solvents[a]

Solvent	η[b]/cp	Φ_f[c]	$\Phi_{t\text{-}c}$	$\Phi_{c\text{-}t}$
Methylcyclohexane	0.69	0.013		
Ethanol	1.2	0.023	0.039	
Glycerol	7.0×10^2	0.048		
Acetonitrile–water[d]			0.048	
Benzene	0.625		0.048	
Chloroform	0.58		0.049	0.029
Acetonitrile	0.345		0.059	

a) 0.001 M 5-SDU at 366 nm. b) At 20 °C from Ref. 25. c) $\lambda_{ex}=318$ nm. d) 70: 30 by volume.

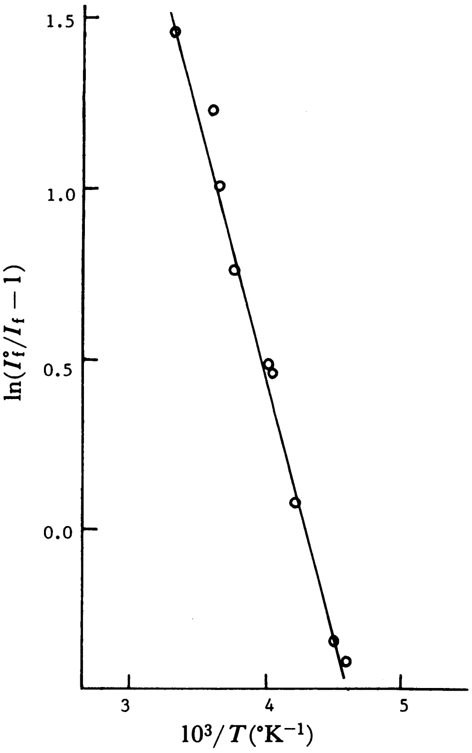


Fig. 1. Arrhenius plot for the temperature dependence of fluorescence intensity of (*E*)-5-styryl-1,3-dimethyluracil in methylcyclohexane–isopentane (1:1, v/v).

The fluorescence quantum yield depends on solvent viscosity (Table 2) and temperature (Fig. 1). If twisting in the first excited singlet state is postulated to be the activated process competing with fluorescence, the suggested mechanism for decay of 5(*E*)-SDU singlet state follows the scheme shown below.

$$\mathrm{t} \xrightarrow{h\nu} {}^1\mathrm{t} \tag{1}$$

$$^1\mathrm{t} \xrightarrow{k_f} \mathrm{t} + h\nu \tag{2}$$

$$^1\mathrm{t} \xrightarrow{k_{ic}} \mathrm{t} \tag{3}$$

$$^1\mathrm{t} \xrightarrow{k_{isc}} {}^3\mathrm{t} \tag{4}$$

$$^1\mathrm{t} \xrightarrow{k_p} {}^1\mathrm{p} \tag{5}$$

$$^1\mathrm{p} \xrightarrow{k_d} \alpha\mathrm{t} + (1-\alpha)\mathrm{c} \tag{6}$$

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† 1 M=1 mol dm^{-3}.

Here, t, c, and p represent trans, cis, and twisted geometry of 5-SDU, while k_f, k_{ic}, k_{isc}, k_p, and k_d are the rate constants for fluorescence, internal conversion, intersystem crossing, twisting, and decay, respectively. The fluorescence quantum yield is given by Eq. 7.

$$\Phi_f = k_f/(k_f + k_{ic} + k_{isc} + k_p) \qquad (7)$$

Since step 5 is temperature dependent, k_p may be described by the Arrhenius equation (Eq. 8),

$$k_p = \mathrm{A}e^{-E_a/RT}. \qquad (8)$$

The limiting fluorescence quantum yield at low temperature where the rate of twisting is too slow to compete with the other decay processes is

$$\Phi_f^0 = k_f/(k_f+k_{ic}+k_{isc}). \qquad (9)$$

Therefore,

$$\frac{\Phi_f^0}{\Phi_f} = \frac{k_f+k_{ic}+k_{isc}+\mathrm{A}e^{-E_a/RT}}{k_f+k_{ic}+k_{isc}}$$

$$\begin{aligned}\ln(\Phi_f^0/\Phi_f-1) &= \ln(I_f^0/I_f-1)\\ &= \ln(\mathrm{A}/(k_f+k_{ic}+k_{isc})) - E_a/RT.\end{aligned}$$

If steps (2), (3), and (4) vs. step (5) is relatively independent of the temperature, plots of $\ln(I_f^0/I_f-1)$ vs. $1/T$ will be linear with a slope of $-E_a/R$. Values for I_f were estimated by modifying the method of Kirby and Steiner[40] and the best straight line relationship was obtained for $I_f^0=79$. An activation energy of 3.0 kcal mol^{-1} (1 cal=4.184 J) for the excited 5(E)-SDU is obtained from the slope.

In the fluorescence excitation polarization with λ_{em} 410 nm in ethanol, the 320 nm band is highly positive polarized ($P_{320\,nm}=0.42$) and flat in the longer wavelength, while the shoulder of 270 nm is relatively little positive polarized ($P_{270\,nm}=0.21$). The fluorescence polarization of 5(E)-SDU with excitation of 320 nm in ethanol is also highly positive polarized. This results imply that the lowest excited singlet state has (π,π^*) configuration in ethanol. 5(Z)-SDU has very weak fluorescence at room temperature, probably due to the fast internal conversion.

5(E)-SDU has very weak phosphorescence with the maxima of 580 and 620 nm in ethanol and isopentane–ethyl ether (1:1, v/v) at 77 K. The phosphorescence polarization of 5(E)-SDU with the excitation of 320 nm in ethanol is highly negative polarized. Accordingly, the lowest triplet state is thought to be $^3(\pi,\pi^*)$ state. Phosphorescence lifetime is shorter in ethanol ($\tau_{ph}=0.38$ s) than in isopentane–ethyl ether (1:1, v/v) ($\tau_{ph}=0.41$ s) and 5(Z)-SDU has no phosphorescence even at 77 K in ethanol.

Direct Photoisomerization. Direct photoisomerization quantum yields of 5-SDU in various solvents are reported in Table 2. The previous papers reported that the photoisomerization and fluorescence of stilbene depends on solvent viscosity[26] and couple with varying temperature in a highly viscous media.[27,28] This was explained by assigning the thermally activated process which competes with fluorescence and leads to isomerization to the twisted form from the fluorescing transoid form.[29] In solvents of low viscosity, there is an inherent thermal barrier to twisting about the central double bond. In certain viscosity regions the solvent imposes an additional barrier which must also be overcome before twisting about take place. Therefore, quantum yield of fluorescence increases and that of trans–cis photoisomerization decreases as solvent viscosity increases.

Both fluorescence and photoisomerization quantum yields of 5(E)-SDU are very low compared to stilbene, probably due to the presence of (n,π^*) state which can lead to very rapid radiationless decay. The photoisomerization quantum yield of 5(E)-SDU is similarly influenced by solvent viscosity (Table 2) as that of fluorescence while it is little affected by the solvent polarity. The energy levels of (π,π^*) and (n,π^*) states in 5-SDU are not close enough to affect the radiationless processes by solvent polarity in contrast to those of StP's.[11b,30] Effect of solvent viscosity suggest the presence of small energy barrier for the internal rotation around the central double bond as calculated in the fluorescence studies.

The quantum yield of cis→trans photoisomerization, $\Phi_{c\rightarrow t}$ of 5(Z)-SDU, is smaller than that of trans→cis photoisomerization, $\Phi_{t\rightarrow c}$ (Table 2) probably due to the shorter lifetime of the excited 5(Z)-SDU compared to 5(E)-SDU and/or to the fast competing reaction, photocyclization. Study of the direct cis–trans photoisomerization is complicated because of the facile photocyclization.[31]

Sensitized Photoisomerization. The quantum yields of benzophenone sensitized photoisomerization for 5-SDU in various solvents are given in Table 3. While the direct photoisomerization is very inefficient, 5-SDU undergoes fairly efficient photoisomerization when sensitized by benzophenone, indicating that the intersystem crossing in 5-SDU does not occur with measurable efficiencies and that the direct and sensitized isomerization pathways probably do not involve a common excited state. The azulene quenching studies lend further support to this contention. As the concentration of benzophenone increases, the photoisomerization quantum yield increases upto certain concentration of benzophenone and then decrease. When the concentration of benzophenone is low, benzophenone molecules do not absorb all the exciting radiation and the yield of the olefin triplet is low while self-quenching and triplet–triplet annihilation of benzophenone[32] becomes significant decreasing the energy transfer to 5-SDU at high benzophenone concentration. As Table 3 shows, the sensitized photoisomerization is strongly affected by the sol-

Table 3. Quantum Yields of Benzophenone-Sensitized Photoisomerization of 5-SDU in Various Solvents[a)]

Solvent	η^b/cp	Concentration of benzophenone/M	$\Phi_{t\to c}$	$\Phi_{c\to t}$	A/A$^{0\,d)}$
Ethanol	1.2	0.05	0.119		0.55
Acetonitrile–Water[c)]		0.05	0.289		0.55
Acetonitrile	0.345	0.05	0.377		0.55
Chloroform	0.58	0	0.049	0.029	1.00
		0.03	0.382		0.67
		0.05	0.393	0.103	0.55
		0.10	0.372		0.38
		0.30	0.230		0.17
Benzene	0.625	0.05	0.403		0.55

a) 0.001 M 5-SDU at 366 nm. b) At 20 °C from Ref. 25. c) 70:30 by volume. d) A/A^0 is the fractions of photons absorbed by 5(*E*)-SDU in these conditions.

vent polarity in contrast to the direct photoisomerization which is affected by the solvent viscosity only. The sensitized photoisomerization quantum yield decreases with increasing the solvent polarity.

This result agrees with the observation that the lifetime of phosphorescence is shorter in the polar solvent than in the nonpolar solvent.

Salt, pH, and Heavy Atom Effect. The photoisomerization and fluorescence of 5(*E*)-SDU are little influenced by proton or salts supporting the results of solvent polarity effect. These results are in contrast with 2- and 4-StP.[30,36–38)] The proton and alkali metal cation are expected to raise the energy level of $^1(n,\pi^*)$ state in the similar manner like the polar solvents. The small Φ_f and short τ_f of 5(*E*)-SDU imply significant contribution of $^1(n,\pi^*)$ state to the lowest excited singlet state and this leads to the reduction of isomerization efficiency occurring in the twisted $^1(\pi,\pi^*)$ state. However, the results of pH and salt effects suggest that the $^1(n,\pi^*)$ level is not close enough to $^1(\pi,\pi^*)$ level and that even though the energy level of $^1(n,\pi^*)$ state is raised by acids and salts, the fluorescent and isomerizable $^1(\pi,\pi^*)$ state is little affected.

Fluorescence of 5(*E*)-SDU is quenched by ethyl iodide and photoisomerization increases with potassium iodide as shown in Table 4 suggesting that the triplet excited state increases due to the enhanced intersystem crossing induced by heavy atoms. The isomerization in the triplet state is more efficient than the direct isomerization as shown in the benzophenone sensitized photoisomerization. The results indicate that direct irradiation does not populate the triplet state significantly and radiative or radiationless deactivation processes from the singlet states determine the photoreactivity of 5-SDU.

Table 4. Heavy Atom Effect on the Fluorescence and Direct trans→cis Photoisomerization of 5(*E*)-SDU in Methanol and Acetonitrile–Water (70:30, v/v), respectively[a)]

Concentration of ethyl iodide/M	I_f^0/I_f[b)]	Concentration of KI/M	$\Phi_{t\to c}$
0	1.00	0	0.043
0.07	1.14	1×10^{-3}	0.041
0.41	1.38	5×10^{-3}	0.040
0.22	1.68	1×10^{-2}	0.048
0.29	1.87	5×10^{-2}	0.052
0.38	2.61	1×10^{-1}	0.103

a) 0.001 M 5(*E*)-SDU. b) I_f^0; the fluorescence intensity in the absence of ethyl iodide. $\lambda_{ex}=318$ nm.

Table 5. Azulene Effect on the Direct and Sensitized Photoisomerization of 5(*E*)-SDU, Stilbene, StP, and BPE[a)]

Compound	Direct $k_q\tau$/M^{-1}	Sensitized[c)] $k_q\tau$/M^{-1}
5(*E*)-SDU[b)]	270	1120
Stilbene	16.1	79
4-Stp	18	130
3,3′-BPE	90	250
4,4′-BPE	70	280

a) Data from Ref. 11b in *t*-butyl alcohol. b) 0.001 M 5(*E*)-SDU in chloroform at 366 nm. c) 0.1 M Benzophenone sensitizer.

Azulene Effect. Azulene quenches only the transoid singlet and triplet states of stilbene on direct and sensitized excitation,[26,39)] but short lived cisoid excited state was not quenched. The following Stern–Volmer equation is derived assuming the selective quenching of transoid excited state by azulene and using the steady state approximation on excited species.

$$\Phi^0_{t\to c}/\Phi_{t\to c} = 1 + k_q\tau[\mathrm{Az}],$$

where, k_q is the diffusion controlled quenching constant, τ is the lifetime of quenched species, and $\Phi^0_{t\to c}$ and $\Phi_{t\to c}$ are trans→cis photoisomerization quantum yields in the absence and presence of azulene, respectively.

Azulene effect on the direct and sensitized photoisomerization of 5(*E*)-SDU is summarized in Table 5. The results show much smaller slope for the direct isomerization compared to that for the benzophenone sensitized isomerization. The same phenomena were observed in the case of stilbene,[26)] StP's, and DPE's.[11b)]

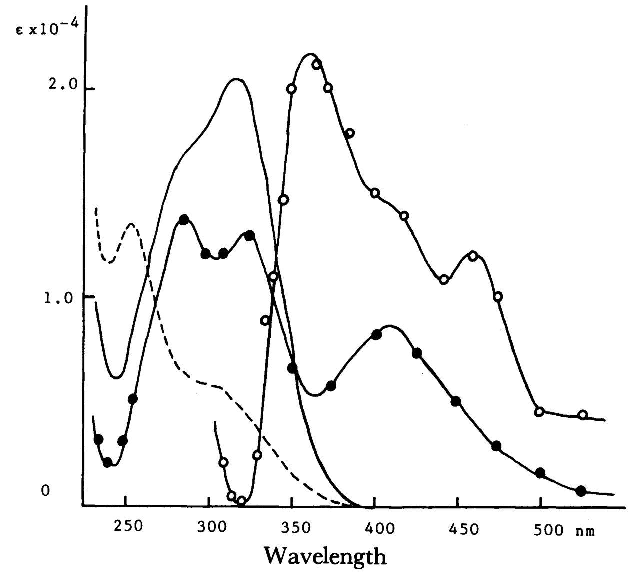

Fig. 2. UV absorption (——; 5(*E*)-SDU, -----; 5-(*Z*)-SDU) and triplet-triplet absorption spectrum (-O-O-O-: 5(*E*)-SDU, -●-●-●-: 5(*Z*)-SDU) of 5-SDU in ethanol.

This is consistent with a singlet mechanism for the direct isomerization.

Laser Flash Photolysis. Nanosecond time-resolved absorption spectra of 5-SDU in ethanol are shown in Fig. 2. In order to determine the molar absorption coefficient for triplet-triplet absorption, benz[*a*]anthracene which has molar absorption coefficient of 2.0×10^4 $M^{-1}cm^{-1}$[†] at 455 nm is used as a reference compound. The intersystem crossing quantum yield, Φ_{isc}, of ca. 0.052 was obtained indicating that intersystem crossing of 5(*E*)-SDU is small but detectable and that the possibility of the involvement of triplet mechanism for direct photoisomerization is very small but cannot be excluded.

Irradiation of *cis*-stilbene in benzene gave only a long-lived absorption centered around 450 nm[34] which was attributed to 9,10-dihydrophenanthrene. Only long-lived transient of 5(*Z*)-SDU is observed at room temperature probably due to the formation of 9,10-dihydrophenanthrene derivative just like in the case of *cis*-stilbene.

The triplet energy of 5(*E*)-SDU was determined by the energy transfer method. Addition of *trans*-stilbene (E_T=50 kcal mol^{-1}) does not affect the transient absorption at 375 nm. With 9,10-diphenylanthracene (E_T=41.8 kcal mol^{-1}), strong triplet-triplet absorption of 9,10-diphenylanthracene at 425 and 480 nm was observed. As benz[*a*]anthracene (E_T=47.2 kcal mol^{-1}) is added, strong triplet-triplet absorption of benz[*a*]anthracene at 475 nm is detected with and without 5(*E*)-SDU. *trans*-1,3,5-Hexatriene gave no effect on the transient absorption curve of 5(*E*)-SDU. From these results, the triplet energy of 5(*E*)-SDU is estimated to lie between 41.8 and 47 kcal mol^{-1}. The plot of log A (absorbance) vs. time (ns) showed the straight line following first-order kinetics. From the decay curve of triplet-triplet absorption, the lifetime of triplet state for 5(*E*)-SDU was determined to be ca. 93 ns. This value is consistent with the triplet lifetime calculated by azulene quenching studies (Table 5) for the sensitized isomerization, assuming the diffusion controlled quenching (k_q=1.2×10^{10} dm^3 mol^{-1} s^{-1} at 20 °C in chloroform).

Conclusion

Fluorescence quantum yield of 5-SDU depends on the temperature and solvent viscosity increasing markedly at low temperature and high viscosity. The proton and salts have no effect on the fluorescence and photoisomerization. Addition of heavy atom affects the intensity of fluorescence and the quantum yield of direct photoisomerization strongly. The large difference is observed in the azulene quenching of the direct and sensitized photoisomerization. These observations strongly indicate the singlet mechanism for the direct photoisomerization and the intersystem crossing is not an important decay path at room temperature even though the laser flash photolysis shows detectable intersystem crossing at room temperature.

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