

PHOTOISOMERIZATION OF 1,2-DIARYLETHYLENES: PHOTOPHYSICAL PROPERTIES OF 5(*E*)-STYRYL-1,3-DIMETHYLURACIL

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Summary

The photophysical properties of 5(*E*)-styryl-1,3-dimethyluracil (5(*E*)-SDU) were investigated. The fluorescence quantum yield and the lifetime are low and short relative to those of the parent aromatic hydrocarbon; this is probably because of the contribution of the n, π^* state to the fast radiationless decay. However, the fluorescence of 5(*E*)-SDU at room temperature is not significantly affected by the solvent polarity, the presence of salts or the pH. This observation indicates that the $^1(n, \pi^*)$ state lies above the lowest $^1(\pi, \pi^*)$ state and that the vibronic mixing between the two states is not extensive. The highly positive fluorescence and the fluorescence excitation polarization confirm that the lowest excited singlet state has the π, π^* configuration. The strong temperature dependence of the fluorescence intensity may be due to the operation of the activated process of twisting in the first excited singlet state competing with fluorescence, and the rotation barrier is estimated to be 3.0 kcal mol⁻¹. The strong quenching of fluorescence intensity by ethyl iodide at room temperature may be indicative of inefficient intersystem crossing. Moreover, only very weak phosphorescence is detected at 77 K and its quantum yield is too low to estimate in either isopentane-ethyl ether (1:1, v/v) or ethanol, supporting the idea of inefficient intersystem crossing suggested by laser flash photolysis results. Therefore, the major radiationless process appears to be internal conversion including rotatory radiationless decay. From the relatively long phosphorescence lifetime and its highly negative polarization the lowest triplet state is considered to be the $^3(\pi, \pi^*)$ state.

1. Introduction

The photophysical and photochemical properties of stilbene-like compounds have been the object of great interest for a long time [1]. The direct

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photoisomerization of stilbene has been proved to occur via an activated internal rotation in the singlet state with the population of the triplet state being negligible.

Heterocyclic compounds containing both n,π^* and π,π^* excited states behave differently from stilbene because of the participation of n,π^* states in the decay and/or reaction processes. It is now strongly suspected that the vibronic perturbation of the lowest energy π,π^* (or n,π^*) singlet state by a close-lying n,π^* (or π,π^*) state leads to an efficient $S_1 \rightsquigarrow S_0$ internal conversion for nitrogen heterocyclic and aromatic carbonyl compounds in the condensed phase [2].

Azastilbenes, typical examples of olefins with a heteroaromatic moiety, have attracted some interest [3, 4]. The styrylpyridines and the 1,2-dipyridylethylenes have very low fluorescence quantum yields when the heteroatom is in the ortho or the para position, owing to the fast deactivation of the excited singlet state through efficient internal conversion rather than a relatively fast rotation [4, 5]. Theoretical calculations show that intersystem crossing is almost negligible in fluid solution, and this has led to the singlet mechanism being proposed for the direct photoisomerization of these molecules; this is further confirmed by the results of laser flash photolysis experiments. Previous reports from our laboratory have shown that 1,2-bis(pyrazinyl)ethylene [6] intersystem crosses efficiently on direct irradiation and that its isomerization proceeds through the triplet manifold, in contrast to stilbene and other aza analogues.

Pyrimidine nucleosides bearing substituents in the 5-position of the heterocyclic ring are biologically significant compounds frequently occurring in nature [7]. 5(*E*)-Styryl-1,3-dimethyluracil (5(*E*)-SDU), in which one phenyl ring in stilbene is replaced by a pyrimidine base, has both n,π^* and π,π^* excited states, in contrast to stilbene, and in this study its photo-physical properties are investigated with respect to the reactive excited states of its photoisomerization.

2. Experimental details

2.1. Materials

5(*E*)-SDU [8] was prepared by the palladium-catalysed reaction [9] between styrene and 1,3-dimethyluracil [10]. The reaction mixture was resolved on a silica-gel column using ethyl acetate-cyclohexane-chloroform (1:1:2, v/v) as the eluent and the product was recrystallized from ethanol. 5(*E*)-SDU in acetonitrile was irradiated for 2 h with benzophenone as the sensitizer in a model RPR 208 Rayonet photochemical reactor equipped with RUL 3500 Å fluorescent lamps, after the solution had been degassed by bubbling with N_2 gas for 1 h. 5(*Z*)-Styryl-1,3-dimethyluracil was separated by column chromatography over silica gel and recrystallized from ethanol.

2.2. Spectroscopic measurements

UV spectra were recorded on a Cary 17 spectrophotometer. The fluorescence lifetime was measured at room temperature with an SLM model 480 phase modulation spectrophotofluorometer. Emission spectra were measured on an Aminco-Bowman spectrophotometer with an Aminco XY recorder at room temperature and at 77 K with modification of the cell compartment. A cylindrical chopper with a maximum rotation frequency of 10 000 rev min⁻¹ with two facing windows was used to isolate the phosphorescence from the other emissions. The phosphorescence lifetime was measured with this instrument, using a mechanical shutter to cut off the excitation light, in conjunction with a Tektronix 5115 storage oscilloscope. The polarized excitation and emission spectra were obtained with a Glan-Prism polarizer and the polarized spectra were corrected by the Azumi-McGlynn formulation [11]. In the measurement of the polarized spectra, short-wavelength cut-off filters [12] were placed in the paths of the exciting and the emitted light, to prevent interference by scattered light. To estimate the temperature dependence of the fluorescence, the temperature of the sample cell was continuously varied from 25 °C to about -150 °C by flowing through cold nitrogen gas and it was maintained to within ±2 °C for recording the spectra. The temperature of the sample solution was measured with a copper-constantan thermocouple. The recorded emission spectra were corrected for the response characteristics of the photomultiplier tube (1P21, S-4 spectral response) and the instrument monochromator as a function of wavelength. The corrected spectra subsequently permitted the determination of the fluorescence quantum yields and the ratios of the phosphorescence quantum yields to the fluorescence quantum yields. The fluorescence quantum yields at room temperature were determined relative to quinine bisulphate ($\Phi_f(298\text{ K}) = 0.55$ in 1.0 N H₂SO₄) or 9,10-diphenylanthracene ($\Phi_f(298\text{ K}) = 1.0$ in cyclohexane) by using the following relationship:

$$\Phi_f = \Phi_f^r \frac{I_s A_r n_r^2}{I_r A_s n_s^2}$$

where Φ_f^r represents the fluorescence quantum yield of the reference and I_s, I_r and A_s, A_r are the integrated areas under the fluorescence spectrum and the absorbance at the exciting wavelength of the sample and the reference respectively, and n_r, n_s are the refractive indices of the solvents for the reference and the sample. In the quantum yield determinations, the absorbance at the excitation wavelength was kept as low as possible, usually below 0.3, in order to minimize errors due to the front surface imprisonment and inner-filter effects. The Aminco-Bowman instrument was also employed to measure the low temperature (77 K) fluorescence quantum yields relative to 9,10-diphenylanthracene ($\Phi_f(77\text{ K}) = 1.0$ in ethanol). The fluorescence quantum yields at 77 K were calculated by the same method used for the room temperature values, assuming that the relative values of the optical densities and refractive indices of all the solutions at 77 K were the same as

at room temperature [13]. The ratios of the phosphorescence quantum yields to the fluorescence quantum yields were estimated by the following correlation:

$$\frac{\Phi_p}{\Phi_f} = \frac{\text{area of phosphorescence}}{\text{area of fluorescence}}$$

2.3. Laser flash photolysis

The nanosecond laser flash photolysis apparatus has been described elsewhere [14]. An XeF (351 nm) and a KrF (248 nm) excimer laser (Lambda Physik EMG101E) were used as the excitation light sources. The concentrations ($(1.5 \times 10^{-5}) - (5.9 \times 10^{-5} \text{ M})$) of 5(*E*)-SDU and 5(*Z*)-SDU were adjusted such that suitable amounts of the laser light were absorbed. The lifetime for decay of the transient of 5(*E*)-SDU was obtained from oscillograms.

3. Results and discussion

The shape and the maximum of the absorption spectrum of 5(*E*)-SDU remain almost unchanged on changing the solvent. The absorption maximum at 318 nm is probably due to the π, π^* band of the conjugated system. The n, π^* band does not appear in the spectrum and seems to be submerged under the more intense π, π^* band. The fluorescence quantum yield of 5(*E*)-SDU is affected by the solvent viscosity rather than by its polarity (see below), and the fluorescence maximum shifts slightly to the long wavelength on increasing the solvent polarity, indicating that the lowest fluorescent state is the $^1(\pi, \pi^*)$ state (in ethanol, $\Phi_f = 0.023$ and $\lambda_{\text{max}}^f = 415 \text{ nm}$; in cyclohexane, $\Phi_f = 0.017$ and $\lambda_{\text{max}}^f = 405 \text{ nm}$ at room temperature). The fluorescence quantum yield and the lifetime of 5(*E*)-SDU are lower and shorter than those of stilbene and the meta isomers of styrylpyridines (StPs) and dipyriddylenes (DPEs) (Table 1). The results imply that the $^1(n, \pi^*)$ state contributes significantly to the lowest excited singlet state. But, as the Φ_f are higher and the τ_f are longer than those of the ortho and the para isomers of StPs and DPEs [15], it is suggested that the $^1(n, \pi^*)$ state in 5(*E*)-SDU is not as delocalized as in 3-StP and 3,3'-DPE, which have near nodes in the meta positions in both π and π^* orbitals which preclude intercombinational transitions between the n, π^* and the lowest π, π^* state and contribute less to radiationless transitions than in 2- and 4-StPs and 2,2'- and 4,4'-DPEs with close-lying π, π^* and n, π^* states.

Protons and alkali metal cations are expected to raise the energy level of the n, π^* state similarly to the polar solvents. The fluorescence of 5(*E*)-SDU is hardly influenced by either protons or salts, in agreement with the results for the effect of solvent polarity. The effects of pH and salts suggest that the $^1(n, \pi^*)$ level is not sufficiently close to the $^1(\pi, \pi^*)$ level and that,

TABLE 1

Fluorescence quantum yields, fluorescence lifetimes and rotation barriers of 5(*E*)-SDU and other stilbene derivatives [5, 15]

Compound	Φ_f	τ_f (ns)	ΔE_f (kcal mol ⁻¹)
5(<i>E</i>)-SDU	0.023 ^a	0.042 ^b	3.0 ^c
Stilbene	0.036	0.09	3.2
2-StP	0.0008	0.007	2.0
3-StP	0.075	0.19	3.3
4-StP	0.0016	0.008	0.8
2,2'-DPE	0.005	—	—
3,3'-DPE	0.13	—	—
4,4'-DPE	0.0004	—	—

^aIn ethanol.

^bAverage value of 50 measurements in ethanol (error limit, ± 7 ps).

^cIn methylcyclohexane-isopentane (1:1, v/v).

even though the energy level of the ¹(*n*, π^*) state is raised by acids and salts, the fluorescent ¹(π , π^*) state is little affected.

The fluorescence of 5(*E*)-SDU is quenched by ethyl iodide, as shown in Table 2, suggesting that the number of molecules in the triplet excited state increases owing to the enhanced intersystem crossing induced by heavy atoms, and direct irradiation does not populate the triplet state significantly.

TABLE 2

Heavy-atom effect on the fluorescence of 5(*E*)-SDU in methanol at room temperature

Concentration of ethyl iodide (M)	I_f^0/I_f^a
0	1.00
0.07	1.14
0.14	1.38
0.22	1.68
0.29	1.87
0.38	2.61

^a I_f^0 and I_f are respectively the fluorescence intensities in the absence and the presence of ethyl iodide at the fluorescence maximum of 415 nm with excitation at 318 nm.

As shown in Table 3, the fluorescence maxima at 77 K are dissimilar to those at room temperature, which exhibit a normal red shift in polar solvents, and they are blue shifted in ethanol relative to isopentane, probably owing to a reduction in charge transfer character by the activation of hydrogen bonding interaction between solvent and solute in the polar protic

TABLE 3

Fluorescence maxima λ_{\max}^f , fluorescence quantum yield Φ_f , phosphorescence maxima λ_{\max}^p , phosphorescence quantum yield Φ_p and phosphorescence lifetime τ_p of 5(*E*)-SDU at 77 K

Solvent	λ_{\max}^f (nm)	Φ_f	λ_{\max}^p (nm)	Φ_p	τ_p (s)
Isopentane	435, 410	0.43	—	—	—
Isopentane-ethyl ether ^a	—	—	580, 620	Very small	0.41
Ethanol	405, 385	0.67	580, 620	Very small	0.38

^a1:1 by volume.

solvent at this low temperature. The fluorescence quantum yield is strongly enhanced on decreasing the temperature from 298 K (fluid) to 77 K (glass) and the phosphorescence quantum yield is very small at 77 K; its maxima remain unchanged on changing the solvent polarity. Therefore, it is suspected that the deactivation of 5(*E*)-SDU at room temperature is mainly attributable to internal conversion rather than to intersystem crossing, and the radiative or radiationless deactivation processes from the singlet states determine the photoreactivity of 5-SDU.

In the fluorescence excitation polarization with $\lambda_{em} = 410$ nm in ethanol, the 320 nm band is highly positive polarized ($P_{320\text{ nm}} = 0.42$) and flat at long wavelengths, while the positive polarization of the shoulder at 270 nm is relatively low ($P_{270\text{ nm}} = 0.21$) (Fig. 1). The fluorescence polarization of 5(*E*)-SDU with excitation at 320 nm in ethanol is also highly positive polarized. Both fluorescence polarization and fluorescence excitation polarization with $\lambda_{ex} = 320$ nm and $\lambda_{em} = 410$ nm respectively, in isopentane-ethyl ether (1:1, v/v), are less polarized than in ethanol but are still positive. These results imply that the lowest excited singlet state has the π, π^* configuration in both ethanol and isopentane-ethyl ether, in agreement with the suggestion above and that the closer proximity of π, π^* to n, π^* in isopentane-ethyl ether leads to the lower polarization. The phosphorescence polarization of 5(*E*)-SDU on excitation at 320 nm in ethanol and isopentane-ethyl ether (1:1, v/v) is highly negative polarized (Fig. 2). Accordingly, the lowest triplet state is thought to be $^3(\pi, \pi^*)$. The phosphorescence lifetime is slightly shorter in ethanol ($\tau_p = 0.38$ s) than in isopentane-ethyl ether ($\tau_p = 0.41$ s) and the observed lifetimes confirm that the lowest triplet state is π, π^* . 5(*Z*)-SDU has very weak fluorescence at room temperature, probably owing to the fast internal conversion, and there is no phosphorescence even at 77 K in ethanol.

The fluorescence quantum yield depends on the solvent viscosity (Table 4) and the temperature (Fig. 3). As the solvent viscosity increases and the temperature decreases, the fluorescence quantum yield increases because of the restrictions on changes in the solute geometry arising from

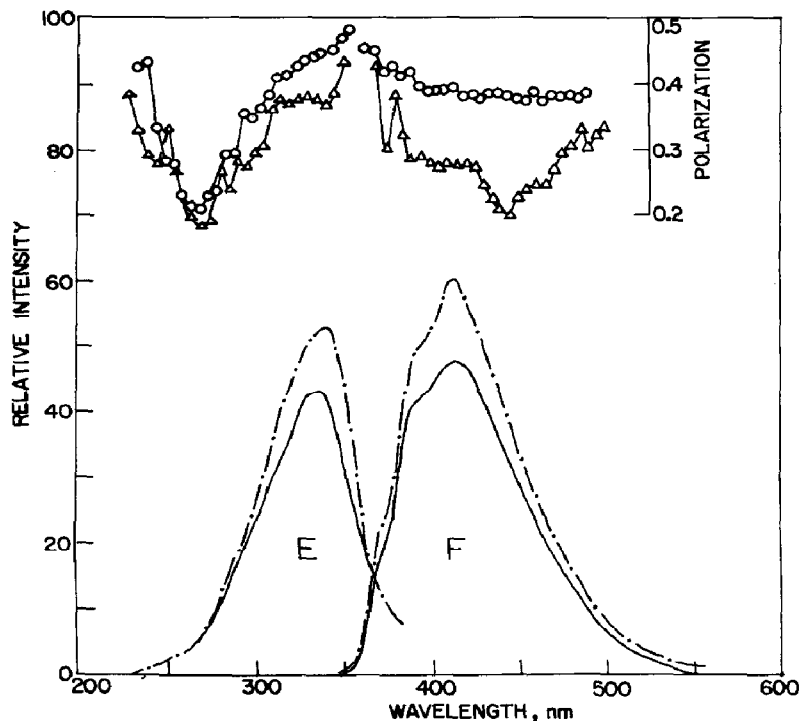


Fig. 1. Fluorescence excitation spectrum, polarized fluorescence excitation with respect to $\lambda_{em} = 410$ nm, fluorescence spectrum and fluorescence polarization with respect to $\lambda_{ex} = 320$ nm of 5(*E*)-SDU in ethanol (— · —, —○—) and isopentane-ethyl ether (1:1, v/v) (—, —△—) at 77 K.

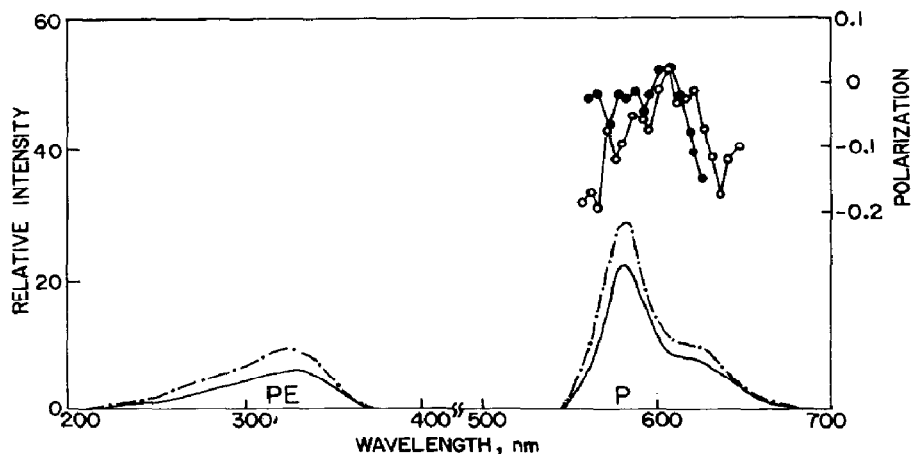


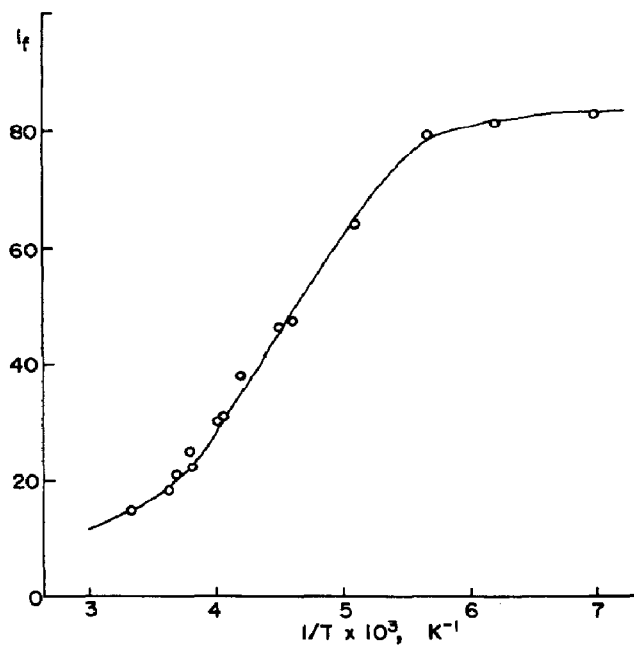
Fig. 2. Phosphorescence excitation spectrum, phosphorescence spectrum and phosphorescence polarization with respect to $\lambda_{ex} = 320$ nm of 5(*E*)-SDU in ethanol (— · —, —○—) and isopentane-ethyl ether (1:1, v/v) (—, —●—) at 77 K.

the low rate at which the solvent cage is capable of rearranging. If twisting in the first excited singlet state, leading to isomerization, is populated and is the thermally activated process competing with fluorescence, the following equations will be applicable:

TABLE 4

Quantum yields of fluorescence of 5(*E*)-SDU in various solvents at room temperature

Solvent	η^a (cP)	Φ_f
Methylcyclohexane	0.69	0.013
Ethanol	1.2	0.023
Glycerin	7.0×10^2	0.048

^aAt 20 °C, from ref. 20.Fig. 3. Temperature dependence of fluorescence intensity for 5(*E*)-SDU in methylcyclohexane-isopentane (1:1, v/v).

t, c and p represent the trans, the cis and the 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

$$\Phi_f = \frac{k_f}{k_f + k_{ic} + k_{isc} + k_p} \quad (I)$$

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

$$k_p = A \exp\left(-\frac{E_a}{RT}\right) \quad (II)$$

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

$$\Phi_f^\circ = \frac{k_f}{k_f + k_{ic} + k_{isc}} \quad (III)$$

Therefore

$$\frac{\Phi_f^\circ}{\Phi_f} = \frac{k_f + k_{ic} + k_{isc} + A \exp(-E_a/RT)}{k_f + k_{ic} + k_{isc}} \quad (IV)$$

$$\ln\left(\frac{\Phi_f^\circ}{\Phi_f} - 1\right) = \ln\left(\frac{I_f^\circ}{I} - 1\right) = \ln\left(\frac{A}{k_f + k_{ic} + k_{isc}}\right) - \frac{E_a}{RT} \quad (V)$$

If steps (2), (3) and (4) vs. step (5) are relatively independent of temperature, plots of $\ln\{(I_f^\circ/I) - 1\}$ 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 [16] and the best straight line relationship was obtained for $I_f^\circ = 79$. An activation energy of $3.0 \text{ kcal mol}^{-1}$ for twisting of the excited 5(*E*)-SDU is obtained from the slope of the plot of $\ln\{(I_f^\circ/I) - 1\}$ vs. $1/T$, as shown in Fig. 4.

The laser irradiation of 5(*E*)-SDU produces a short-lived transient considered to be the triplet species. Nanosecond time-resolved transient absorption spectra for the UV region were obtained with the *E* and *Z* isomers of 5-SDU in ethanol at room temperature as shown in Fig. 5. In order to determine the molar absorption coefficient for triplet-triplet absorption, 1,2-benzanthracene, which has a molar absorption coefficient of $2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 455 nm, was used as a reference compound. An intersystem crossing quantum yield Φ_{isc} of about 0.052 was obtained.

The triplet state of stilbene is not populated in fluid solution at room temperature and this is consistent with the singlet mechanism for the direct photoisomerization of stilbene [17, 18], but the triplet-triplet absorption of stilbene in glassy frozen solution at 77 K is observed by nanosecond laser flash photolysis [19]. In contrast with stilbene, several nitro-substituted

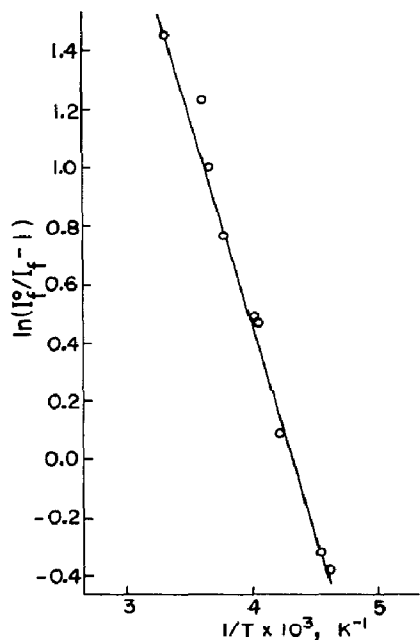


Fig. 4. Arrhenius plot for 5(*E*)-SDU in methylcyclohexane-isopentane (1:1, v/v).

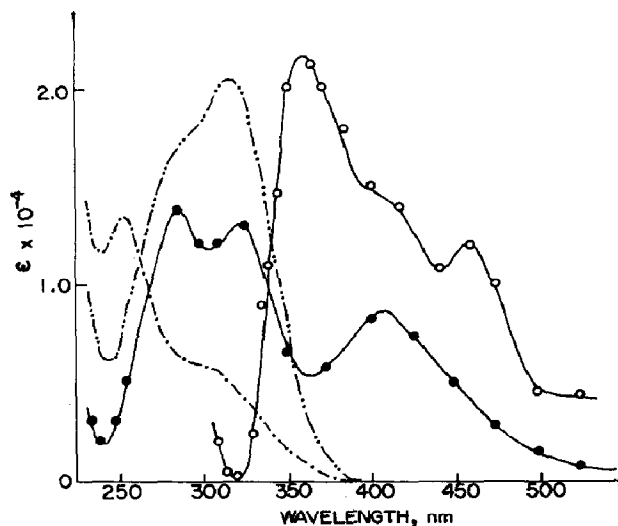


Fig. 5. UV absorption (---, 5(*E*)-SDU; - · -, 5(*Z*)-SDU) and triplet-triplet absorption spectrum (—○—, 5(*E*)-SDU; —●—, 5(*Z*)-SDU) of 5-SDU in ethanol.

stilbenes [17, 18] have strong short-lived transient absorption at room temperature on laser flash photolysis. The transients are identified as the triplet states of the nitrostilbenes. Nitro groups enhance the $^1S \rightsquigarrow T$ transition rate without changing the $T \rightsquigarrow ^0S$ transition rate appreciably, owing to the participation of the n, π^* state in the decay processes. The enhancement of the intersystem crossing rate leads to an increase in the population of the triplet state, and thus allows the transient to appear.

The triplet-triplet absorption of 5(*E*)-SDU, with its absorption maximum at about 360 nm, is stronger than that of stilbene but is very weak in comparison with the nitro-substituted stilbenes. This indicates that the intersystem crossing of 5(*E*)-SDU at room temperature is inefficient and that the probability of the involvement of triplet route for reaction, e.g. photoisomerization, on direct irradiation is very low.

The shape and the maxima of the transient absorption spectrum of 5(*Z*)-SDU shown in Fig. 5 differ from those of 5(*E*)-SDU. It has been reported that irradiation of a 1.0 M solution of *cis*-stilbene in benzene gave only a long-lived absorption centred around 450 nm which was attributed to the formation of dihydrophenanthrene during laser flash photolysis [17]. The flash photolysis of 5(*Z*)-SDU shows no typical decay curve within 500 ns and only a long-lived transient is observed at room temperature, probably from the formation of a dihydrophenanthrene derivative during the laser flash photolysis, just as in the case of *cis*-stilbene.

The energy transfer method (nanosecond spectroscopy) was utilized to determine the energy of the triplet state of 5(*E*)-SDU. Addition of *cis*-stilbene ($E_T = 50 \text{ kcal mol}^{-1}$) does not affect the transient absorption curve of 5(*E*)-SDU at 375 nm. On adding 9,10-diphenylanthracene ($E_T = 41.8 \text{ kcal mol}^{-1}$), strong triplet-triplet absorption of 9,10-diphenylanthracene is observed at 425 nm and 480 nm. As benzanthracene ($E_T = 47.2 \text{ kcal mol}^{-1}$) is added, strong triplet-triplet absorption of benzanthracene at 475 nm is detected both with and without 5(*E*)-SDU. *trans*-1,3,5-Hexatriene ($E_T = 47.0 \text{ kcal mol}^{-1}$) had 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.

From the decay curve of triplet-triplet absorption of 5(*E*)-SDU, the plot of the log of the absorbance vs. time (in nanoseconds) after the flash photolysis gives a straight line following first-order kinetics, as shown in Fig. 6, and the triplet lifetime of 5(*E*)-SDU is determined to be about 93 ns from the slope.

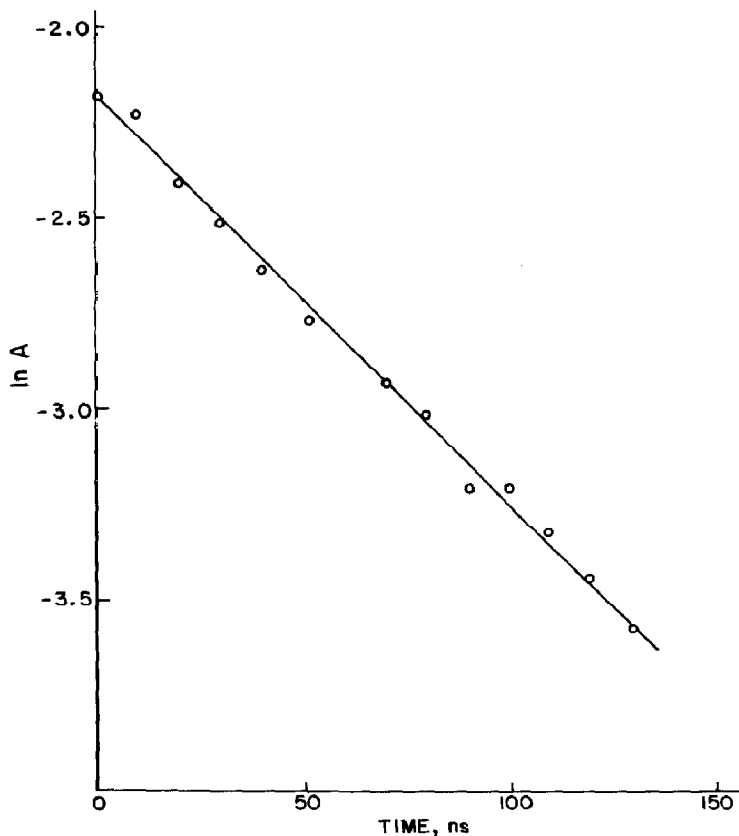


Fig. 6. Plot of $\ln(\text{absorbance})$ vs. time from the triplet decay curve of 5(*E*)-SDU at 376 nm in ethanol.

4. Conclusions

The absorption spectrum is nearly independent of the solvent. The fluorescence quantum yield is affected by the viscosity of the solvent rather than by its polarity. The fluorescence and the fluorescence excitation polarization are highly positive polarized. These results suggest that the lowest excited singlet state is the $^1(\pi, \pi^*)$ state. The relatively weak fluorescence and the short fluorescence lifetime imply that a significant contribution of the n, π^* state is introduced by the heteroatom to the lowest excited singlet state, leading to fast internal conversion. However, the effect of the solvent polarity, salts and pH on the fluorescence is negligible, implying that there is a considerable energy gap between the $^1(n, \pi^*)$ state and the lowest $^1(\pi, \pi^*)$ state. The fluorescence intensity is found to increase sharply with increasing solvent viscosity and decreasing temperature. This indicates that a potential barrier, estimated to be $3.0 \text{ kcal mol}^{-1}$, is situated between the first excited singlet level and the active intermediate responsible for twisting. The fluorescence is strongly quenched by ethyl iodide. The phosphorescence at 77 K and the triplet-triplet absorption at room temperature are very weak, indicating that direct irradiation does not populate the triplet state significantly and that internal conversion rather than intersystem crossing is the major process in the deactivation of the singlet state at room temperature. Therefore it is concluded that decay and/or reaction (such as isomerization) processes from the singlet state determine the photo-reactivity of 5(E)-SDU. As the phosphorescence lifetime is relatively long and the phosphorescence polarization is highly negative polarized, it is deduced that the lowest triplet state has the π, π^* configuration.

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