

NANOSECOND LASER FLASH PHOTOLYSIS STUDY OF 1,2-BISPYRAZYLETHYLENE

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Summary

The nanosecond laser flash photolysis of 1,2-bispyrazylethylene indicates that an efficient intersystem crossing occurs on direct excitation. The triplet energy level of the trans isomer lies close to $39.0 \text{ kcal mol}^{-1}$ and that of the cis isomer lies between 35.1 and $39.0 \text{ kcal mol}^{-1}$. The triplet-triplet absorption maximum of the trans isomer is blue shifted and the absorption spectra show fine structure because of the change of the energy gap between the $^3(n,\pi^*)$ and the lowest $^3(\pi,\pi^*)$ state as the polarity of the medium increases. The triplet lifetime of the trans isomer (160 ns) directly measured by laser flash photolysis also indicates that the direct photoisomerization of this compound proceeds through the triplet manifold in contrast to the behaviour observed for stilbene.

1. Introduction

The photochemical reactions of stilbenes have been studied extensively and the photoisomerization mechanism in which the unsubstituted stilbene isomerizes in the singlet manifold is well established [1]. The triplet states of stilbenes were observed in transient absorptions by several groups [2, 3] in glassy frozen solutions at 77 K. Herkstroeter and McClure [3] and Görner and Schulte-Frohlinde [4] also studied the triplet-triplet absorption of stilbenes via flash photolysis. By employing a model in which azulene quenches $^3p^*$ to the trans ground state (0t) [1, 5 - 7], a quenching rate constant of $4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and an effective triplet lifetime of about 120 ns have been estimated. This triplet lifetime is in agreement with the results obtained using pulse radiolysis [8] and sensitized laser photolysis [9].

More recently, however, Görner and Schulte-Frohlinde [10] and Caldwell [11] showed that the lifetime of the triplet state of unsubstituted *trans*-stilbene is 60 ns.

The photochemical behaviour and spectroscopy of nitrogen-containing heterocyclic compounds have also been investigated [12]. Nonetheless, the mechanistic details of the photoisomerization have been the subject of considerable controversy [13,14]. The introduction of nitrogen atoms into the phenyl rings significantly affects the photochemical and photophysical behaviour of stilbene because of the proximity of the n,π^* state to the lowest π,π^* state in these compounds in the reaction mechanism.

1,2-Bispyrazylethylene (BPyE) is a tetraazastilbene in which the phenyl rings of stilbene are replaced by two pyrazine rings. In this investigation, we studied the photophysical and photochemical behaviour of the excited triplet states of BPyE by means of nanosecond laser flash photolysis. The main purpose of this study is to elucidate the mechanism of the photoisomerization of BPyE.

2. Experimental details

2.1. Materials

trans-BPyE was prepared by a previously reported method [15] which involved the condensation of methyl pyrazine with pyrazine aldehyde, and was recrystallized from acetone. The *cis* isomer was prepared by irradiation of the *trans* isomer followed by separation on a silica gel column and then recrystallization from cyclohexane.

2.2. Laser flash photolysis

The nanosecond laser flash photolysis apparatus was used as described elsewhere [16]. The laser flash photolysis experiments were carried out by using XeF (351 nm) and KrF (248 nm) excimer lasers (Lambda Physik EMG 101E) as the sources of the exciting light. Transient species were monitored using a pulsed XeF lamp. The monitor light was divided into two beams after passage through the sample cell. One beam was routed through a Jobin-Yvon H20UVL monochromator; with this the absorbance at 376 nm (for the *trans* isomer) was monitored for each laser shot and was used to normalize the spectrum. The detectors were Hamamatsu R758 photomultipliers. The signals were displayed on a Tektronix R7834 oscilloscope with 7A26 and 7B80 time bases and on a Tektronix R466 oscilloscope. The time resolution of the total system was about 10 ns. A Tektronix differential comparator (7A13) was used for measurements of the triplet-triplet absorption spectrum and the relaxation rates of BPyE. The time resolution was about 15 ns.

The concentrations ($(1.0 - 2.0) \times 10^{-5}$ M) of *trans*- and *cis*-BPyE were adjusted so that suitable amounts of laser light were absorbed. The lifetimes for the decay of the transient and the ground state depletion of BPyE were directly obtained from oscillograms.

3. Results and discussion

3.1. Transient profiles

The following processes are generally considered to describe the trans \rightleftharpoons cis photoisomerization on laser flash photolysis.

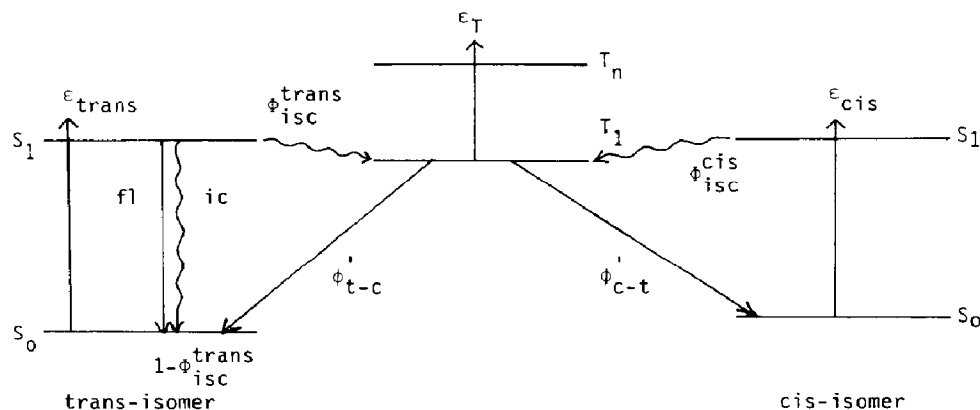


Fig. 1. Radiative and non-radiative processes in trans \rightleftharpoons cis photoisomerization on laser flash photolysis.

As shown in Fig. 1, the lowest excited singlet state returns to the ground state via fluorescence and internal conversion and forms the lowest triplet state through intersystem crossing within a time corresponding to the lifetime. All the triplet states formed decay through intersystem crossing to the trans and cis ground states, *i.e.*

$$\begin{aligned} \phi_{t \rightarrow c}' + \phi_{c \rightarrow t}' &= 1.0 \\ \Phi_{t \rightarrow c}^{\text{obs}} &= \Phi_{\text{isc}}^{\text{trans}} \phi_{t \rightarrow c}' \end{aligned} \quad (1)$$

where $\Phi_{t \rightarrow c}^{\text{obs}}$ is the observed quantum yield of trans \rightarrow cis isomerization, $\phi_{t \rightarrow c}'$ is the fraction of triplet states that decay to the cis ground state ($\phi_{t \rightarrow c}'$ is obtained by direct and sensitized photoisomerization of BPyE in solution: $\phi_{t \rightarrow c}' = 0.43$ [17]) and $\Phi_{\text{isc}}^{\text{trans}}$ is the quantum yield of intersystem crossing for the trans isomer.

From Fig. 1, the difference absorption coefficient $\Delta\epsilon_{\text{obs}}(t)$ (the difference between absorption after decay and ground state absorption (initial absorption) on laser flash photolysis) may be calculated using the equations

$$\begin{aligned} \Delta\epsilon_{\text{obs}}(t) &= \Phi_{\text{isc}}^{\text{trans}} \epsilon_T e^{-t/\tau_T} + \Phi_{\text{isc}}^{\text{trans}} \phi_{t \rightarrow c} \epsilon_{\text{cis}} (1 - e^{-t/\tau_T}) + \\ &+ \epsilon_{\text{trans}} \Phi_{\text{isc}}^{\text{trans}} \phi_{t \rightarrow c}' (1 - e^{-t/\tau_T}) + \epsilon_{\text{trans}} (1 - \Phi_{\text{isc}}^{\text{trans}}) - \epsilon_{\text{trans}} \end{aligned} \quad (2)$$

$$= \Phi_{\text{isc}}^{\text{trans}} (\epsilon_T - \epsilon_{\text{trans}}) e^{-t/\tau_T} + \Phi_{t \rightarrow c}^{\text{obs}} \Delta\epsilon_{c-t} (1 - e^{-t/\tau_T}) \quad (3)$$

where ϵ_T is the absorption coefficient of triplet-triplet absorption of the trans isomer, ϵ_{trans} and ϵ_{cis} are the absorption coefficients of ground state absorption of the trans and cis isomers respectively, t is the scanning time

of the oscillogram for the transient absorption, τ_T is the lifetime of the triplet state for the trans isomer and $\Delta\epsilon_{c-t}$ is the difference in absorption coefficient between cis and trans ground state absorptions ($\Delta\epsilon_{c-t} = \epsilon_{cis} - \epsilon_{trans} \approx -8000 \text{ M}^{-1} \text{ cm}^{-1}$ for BPyE at 344 nm).

In eqn. (2), the first term is the triplet-triplet absorption of the trans form after intersystem crossing, the second and third terms are the ground state absorption of the cis form after isomerization and the trans form after decay from the triplet state, the fourth term is the ground state absorption of the trans form after decay from the excited singlet state, and the fifth term is the initial laser flash absorption by the ground state trans isomer.

The difference absorbance $\Delta A_{obs}(t)$ between the absorption after decay and the initial ground state absorption in Fig. 1 can be obtained directly from the oscillograms obtained on laser flash photolysis.

$$\Delta A_{obs}(t) = \Delta\epsilon_{obs}(t)C_e l \quad (4)$$

where C_e is the concentration of molecules in the excited singlet state ($C_e = 8.33 \times 10^{-6} \text{ M}$) and l is the path length of the sample cell ($l = 3.8 \text{ cm}$).

In order to determine the difference absorption coefficient $\Delta\epsilon_{obs}(t)$ at each wavelength, 1,2-benzanthracene (BA) was used as a reference compound. The ratio of Abs^{BA} at 455 nm (at $t = 250 \text{ ns}$) to $\text{Abs}^{t\text{-BPyE}}$ at 376 nm (at $t = 0$) was measured as 0.357 under the same conditions, where

$$\text{Abs}^{BA}(\text{triplet state on laser flash photolysis}) = \epsilon_{isc}^{BA} \epsilon_T^{BA} C_e l$$

and

$$\text{Abs}^{t\text{-BPyE}}(\text{triplet state on laser flash photolysis}) = \Phi_{isc}^{t\text{-BPyE}} \epsilon_T^{t\text{-BPyE}} C_e l$$

The molar extinction coefficient ϵ_T^{BA} of triplet-triplet absorption of BA at 455 nm is $2.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and $\Phi_{isc}^{BA} = 0.79$ [18, 19]; therefore

$$\begin{aligned} \Delta\epsilon_{obs}^{t\text{-BPyE}}(376 \text{ nm}) &= \Phi_{isc}^{t\text{-BPyE}} \epsilon_T^{t\text{-BPyE}} \\ &= 0.357 \times 0.79 \times 2.0 \times 10^4 \\ &= 5640 \text{ M}^{-1} \text{ cm}^{-1} \end{aligned} \quad (5)$$

The difference absorption coefficient at each wavelength for *trans*-BPyE can be obtained after normalization by using the value of $5640 \text{ M}^{-1} \text{ cm}^{-1}$ at 376 nm as a reference.

3.2. Determination of quantum yields of *trans* \rightleftharpoons *cis* isomerization and intersystem crossing

The quantum yields of *trans* \rightleftharpoons *cis* isomerization and intersystem crossing are obtained by the following method. At $t = 0$ (i.e. immediately after flash photolysis), eqn. (3) becomes eqn. (6):

$$\Delta\epsilon_{obs}(t = 0) = \Phi_{isc}^{t\text{-BPyE}} (\epsilon_T^{t\text{-BPyE}} - \epsilon_{trans}) \quad (6)$$

For *trans*-BPyE, $\Delta\epsilon_{obs}(t = 0)$ is found to be zero at 344 nm in methanol and at 286 nm in *n*-hexane, meaning that $\epsilon_T^{t\text{-BPyE}}$ is equal to ϵ_{trans} at these

wavelengths. Because the rate of intersystem crossing is very fast ($3.5 \times 10^9 \text{ s}^{-1}$) compared with our time resolution (about 15 ns), triplet–triplet absorption just after intersystem crossing is practically observed at $t = 0$.

At $t = \infty$ (i.e. at the point of complete decay of the triplet–triplet absorption) and at wavelengths where $\epsilon_{\text{T}}^{t\text{-BPyE}} = \epsilon_{\text{trans}}$, we can derive eqn. (7) from eqn. (3):

$$\Delta\epsilon_{\text{obs}}(t = \infty) = \Phi_{\text{t} \rightarrow \text{c}}^{\text{obs}} \Delta\epsilon_{\text{c} \rightarrow \text{t}} \quad (7)$$

Under these conditions, $\Delta\epsilon_{\text{obs}}(t = \infty)$ for *trans*-BPyE is calculated using eqn. (5) to be $-3386 \text{ M}^{-1} \text{ cm}^{-1}$ at 344 nm in methanol and $-1939 \text{ M}^{-1} \text{ cm}^{-1}$ at 286 nm in *n*-hexane. The quantum yields of *trans* \rightarrow *cis* isomerization via the triplet surface at these wavelengths can be calculated using eqn. (7) which gives $\Phi_{\text{t} \rightarrow \text{c}}^{\text{obs}} = 0.42$ in methanol at 344 nm and $\Phi_{\text{t} \rightarrow \text{c}}^{\text{obs}} = 0.24$ in *n*-hexane at 286 nm. From these values of $\Phi_{\text{t} \rightarrow \text{c}}^{\text{obs}}$ the quantum yields of intersystem crossing can be obtained from eqn. (1). The intersystem crossing yield $\Phi_{\text{isc}}^{t\text{-BPyE}}$ of *trans*-BPyE obtained using this method was 0.98 in methanol and 0.56 in *n*-hexane. The quantum yields of *cis* \rightarrow *trans* isomerization and intersystem crossing for *cis*-BPyE were determined in the same way and the values $\Phi_{\text{c} \rightarrow \text{t}}^{\text{obs}} = 0.19$ and $\Phi_{\text{isc}}^{c\text{-BPyE}} = 0.34$ in methanol were obtained.

These quantum yields for *trans* \rightarrow *cis* isomerization and intersystem crossing for *trans*-BPyE determined from laser flash experiments at room temperature (controlled at $24 \pm 1 \text{ }^\circ\text{C}$) were about the same as those determined from the quantum yields of direct and sensitized photoisomerization in solution [17]. The quantum yields of direct (at 366 nm) and biacetyl-sensitized (at 435.8 nm) *trans*–*cis* photoisomerization of BPyE are 0.23 and 0.41 in benzene ($\Phi_{\text{isc}}^{t\text{-BPyE}} = 0.56$) and 0.42 and 0.43 in methanol ($\Phi_{\text{isc}}^{t\text{-BPyE}} = 0.98$) respectively. The quantum yields of direct and biacetyl-sensitized *cis*–*trans* photoisomerization of BPyE are 0.05 and 0.56 in methanol and $\Phi_{\text{isc}}^{\text{BPyE}} = 0.11$. The quantum yields obtained for *cis*-BPyE by laser flash photolysis, however, are different from the values obtained from direct and sensitized photoisomerization in solution [17] because the *cis*–*trans* isomerization process competes with the very efficient formation of *cis*-DHP (DHP \equiv 4*a*,4*b*-dihydrophenanthrene derivative: the photocyclization product).

3.3. Lifetime of the triplet state

The plot of $\ln(\Delta\text{Abs}(t))$ versus t/τ_{T} obtained using eqns. (3) and (4) shows good linearity. We can calculate the lifetime of the triplet state from the slope of this plot (Fig. 2). The triplet decay (triplet–triplet absorption) curves (at 376 nm for *trans*-BPyE) are exactly matched by the ground state depletion curves (at 344 nm for *trans*-BPyE) measured in methanol using laser flash photolysis and give the same value of 160 ns for the decay time of *trans*-BPyE at room temperature. The triplet lifetime of *trans*-BPyE obtained using laser photolysis is exactly the same as the triplet lifetime obtained from azulene quenching studies in solution [17]. The same Stern–Volmer constant ($1.4 \times 10^3 \text{ M}^{-1}$) was obtained in the azulene quenching of direct

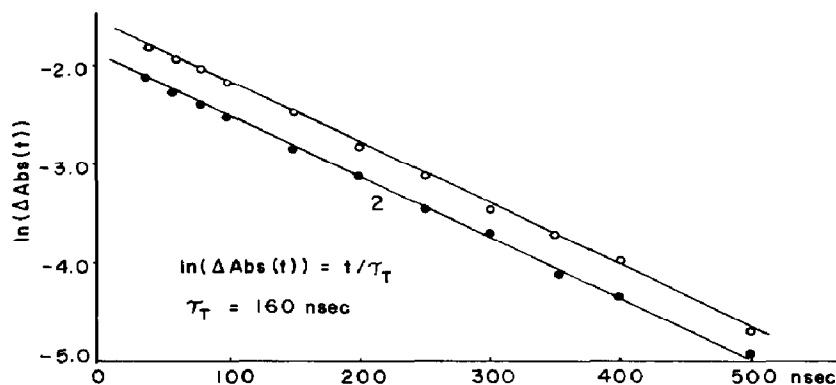


Fig. 2. Plot of $\ln(\Delta \text{Abs}(t))$ vs. time (oscilloscope scanning time): curve 1, triplet decay curve of *trans*-BPyE at 376 nm; curve 2, depletion curve of ground state *trans*-BPyE at 344 nm in methanol.

and sensitized *trans* \rightarrow *cis* photoisomerization of BPyE in benzene–dichloromethane (1:1 by volume). Assuming that azulene quenches BPyE triplets with a rate that is diffusion controlled, the triplet lifetime is calculated to be 160 ns. These observations must be direct evidence for a mechanism in which the *trans* \rightleftharpoons *cis* photoisomerization of BPyE proceeds via a triplet surface.

3.4. Energy level of the triplet state

The triplet energy of BPyE was measured by means of the energy transfer method utilizing nanosecond laser spectroscopy. 9,10-Diphenylanthracene ($E_T = 41.8 \text{ kcal mol}^{-1}$) has no effect on the transient absorption of *trans*- and *cis*-BPyE at 370 nm and 480 nm respectively, but perylene ($E_T = 35.1 \text{ kcal mol}^{-1}$) has a strong influence. However, when azulene ($E_T = 39.0 \text{ kcal mol}^{-1}$) is added, the decay rate of *trans*-BPyE increases but the decay rate of the *cis*-BPyE transient is not affected. These results suggest that the triplet energy level of *trans*-BPyE lies close to $39.0 \text{ kcal mol}^{-1}$ and that of *cis*-BPyE lies between 35.1 and $39.0 \text{ kcal mol}^{-1}$.

3.5. Transient spectra and solvent shifts of triplet–triplet absorption spectra

Nanosecond time-resolved absorption spectra for the UV region were measured with *trans*- and *cis*-BPyE in methanol or in *n*-hexane at room temperature as shown in Figs. 3 - 6 together with the UV spectrum (ground state absorption). The plot of $\Delta\epsilon_{\text{obs}}$ versus wavelength from eqn. (3) shows the difference absorption spectra in units of relative optical density. The plot of ϵ_T versus wavelength from eqn. (6) also shows the triplet–triplet absorption spectra. The triplet–triplet absorption coefficients determined from eqn. (6) are listed in Table 1 together with the absorption maxima of the stilbenes.

Herkstroeter and McClure [3] observed the triplet–triplet absorption of stilbenes in a rigid glass at 77 K using flash photolysis but could not observe the triplet–triplet absorption in fluid solutions at room temperature.

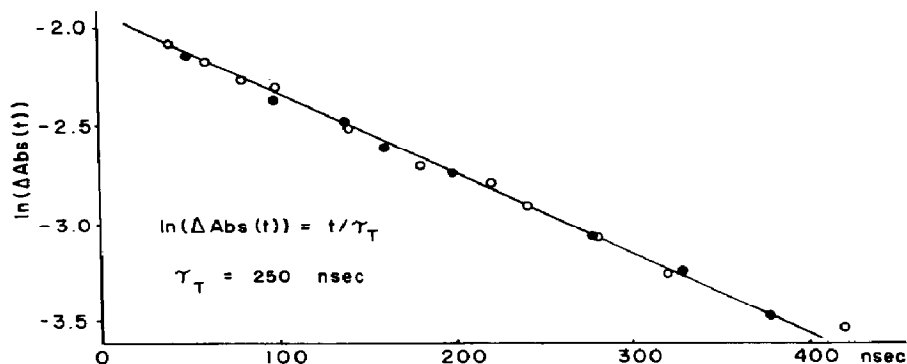


Fig. 3. Plot of $\ln(\Delta \text{Abs}(t))$ vs. time (oscilloscope scanning time): \circ , triplet decay curve of *cis*-BPyE at 676 nm; \bullet , depletion curve of ground state *cis*-BPyE at 303 nm in methanol.

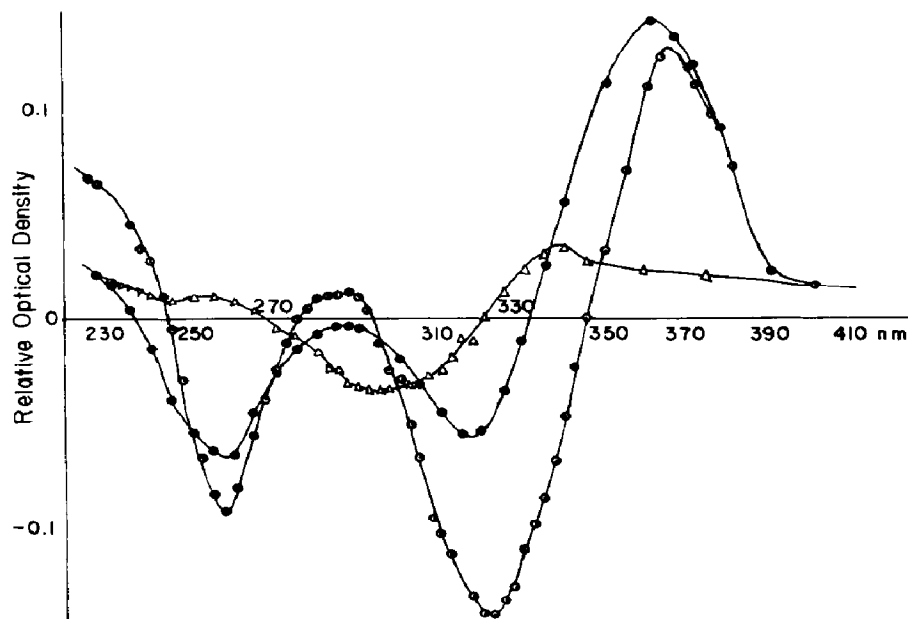


Fig. 4. Short-lived transient absorption spectra (difference absorption spectra) at $t = 0$ (i.e. immediately after flash photolysis): \bullet , *trans*-BPyE in *n*-hexane; \circ , *trans*-BPyE in methanol; Δ , *cis*-BPyE in methanol.

By means of sensitized nanosecond time-resolved absorption spectroscopy, the triplet state of stilbene was observed in fluid solutions with a lifetime of about 60 ns [10, 11]. Furthermore, a quantum yield for intersystem crossing of 0.2 has been reported recently for stilbene in glycerol at room temperature [20]. In contrast to unsubstituted stilbene, nitroaromatics very often only show phosphorescence and not fluorescence. Several nitro-substituted stilbenes have been shown to possess strong short-lived transient absorptions at room temperature by using laser flash photolysis [21]. In the presence of nitro substituents, intersystem crossing is enhanced to such

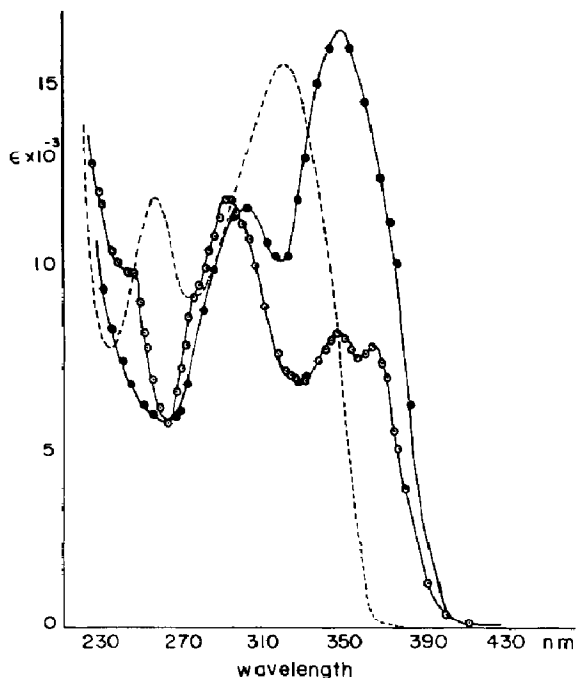


Fig. 5. UV absorption spectrum (---) and triplet-triplet absorption spectrum of *trans*-BPyE in *n*-hexane (●) and in methanol (○).

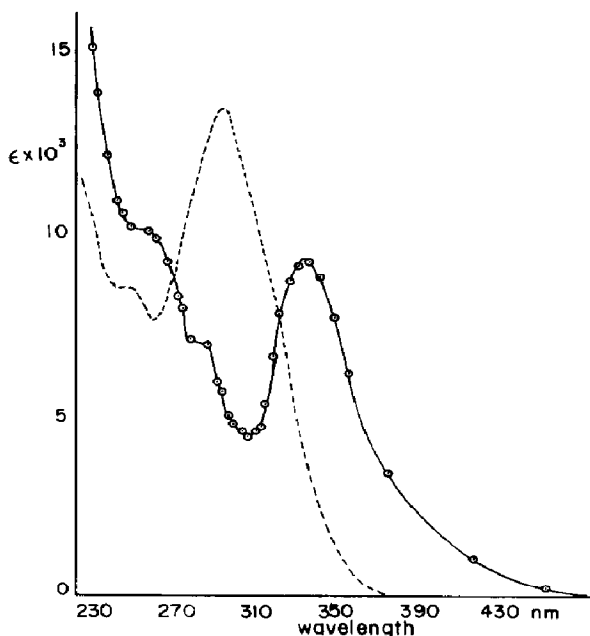


Fig. 6. UV absorption spectrum (---) and triplet-triplet absorption spectrum of *cis*-BPyE (○) in methanol.

TABLE 1

Molar extinction coefficients of maximum triplet-triplet absorption bands of BPyE

Substance	Wavelength (nm)	ϵ_T ($M^{-1} \text{ cm}^{-1}$)
<i>trans</i> -Stilbene ^a	378	3.4×10^4
<i>trans</i> -Stilbene- <i>d</i> ₁₂ ^a	378	2.8×10^4
4,4'-Dichlorostilbene ^a	359	2.8×10^5
<i>cis</i> -BPyE ^b	336	9.2×10^3
<i>trans</i> -BPyE ^b	291	1.2×10^4
	346	8.2×10^3
	363	7.8×10^3
	301 ^c	1.2×10^4
	356 ^c	1.6×10^4

^aFrom ref. 3.

^bOur experimental results in methanol at room temperature.

^cIn *n*-hexane at room temperature.

a degree that the triplet states are highly populated. The enhancement of intersystem crossing is entirely associated with the participation of the n, π^* state of the nitro groups in the decay processes. The charge transfer charac-

ter of the excited states of nitro-substituted stilbenes does not seem to influence intersystem crossing, as indicated by *p*-cyano-*p'*-methoxystilbene which lacks a nitro group and shows no transient at room temperature and a much weaker triplet-triplet absorption even at low temperatures [22].

The transient species of stilbene generated using flash photolysis in glassy matrices at 77 K have previously been identified as triplet states [2 - 4]. We observed strong triplet-triplet absorption for the *trans* form in fluid solutions at room temperature just as in the nitro-substituted stilbenes [21, 22] in which the nitro groups enhance the rate of intersystem crossing. The transient spectra (difference absorption spectra) of *trans*-BPyE in non-polar and polar media show similar shapes and absorption maxima (Fig. 3) to those of nitro-substituted stilbenes [21]. The solvent shift of the triplet-triplet absorption in nitro-substituted stilbenes is unusually large and is accompanied by a change in shape of the absorption spectra. In order to explain the solvent shift, Gegiou *et al.* [23] assumed that the lowest triplet state for the nitro-substituted stilbenes changes from $^3(n,\pi^*)$ to $^3(\pi,\pi^*)$ in character as the solvent polarity increases. In the flash photolysis of BPyE, the triplet-triplet absorption maximum is blue shifted as the polarity of the medium increases (Fig. 4). The triplet-triplet absorption spectra also show fine structure and their shapes change as the medium is changed from *n*-hexane to methanol. These effects may be due to the increase of the energy gap between the $^3(n,\pi^*)$ state and the lowest $^3(\pi,\pi^*)$ state as the polarity of the medium increases, in contrast to nitro-substituted stilbenes.

3.6. Mechanism of *trans* \rightleftharpoons *cis* isomerization

Bent and Schulte-Frohlinde [21] explained that the *cis* \rightarrow *trans* isomerization of substituted stilbenes, especially nitro-substituted stilbenes, occurs in the excited singlet state by rotation about the C=C double bond since the lifetime of the transient species (the excited singlet state) of the *cis* isomer is extremely short [24] and it is most unlikely that during this time intersystem crossing can occur. The reason for the short lifetime of the *cis* isomer in the excited singlet state is believed to be the steepness of the potential curve for unsubstituted stilbene as calculated by Borrell and Greenwood [25], in contrast to the flat minimum in the excited singlet state of the *trans* isomer. In contrast to stilbene, however, the absence of an energy barrier between the *transoid* state and the rotated minimum state or any other state, such as the triplet state, is observed for BPyE in laser flash photolysis studies. The large quantum yields of intersystem crossing and the triplet lifetime observed must be direct evidence for a *trans* \rightleftharpoons *cis* isomerization mechanism via the triplet state. From these results, therefore, it is concluded that the transient of BPyE is a triplet state and direct *trans* \rightleftharpoons *cis* photoisomerization of BPyE proceeds through the triplet excited state in contrast to the behaviour of stilbene.

Acknowledgment

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