123–124 °C; **24** (petroleum ether), 13.5 mg, mp 95–96 °C; **25** (petroleum ether–CH$_2$Cl$_2$) 50 mg, mp 121–122 °C.

(b) 100% Conversion. After standing 24 h the 200-mL aliquot was filtered, as earlier, into a solution of 4.5 g (0.114 mol) of NaOH in 15 mL of water, giving 400 mg (1.59 mmol, 39.7%) of **20**. The filtrate was worked up exactly as before but without prior air bubbling. Flash chromatography gave 19 mg (0.08 mmol, 1.8%) of **20** (fractions 1–4), 92 mg (0.28 mmol, 6.8%) of **24** (fractions 8–10), 500 mg (2.24 mmol, 27.3%) of **23** (fractions 13–27), and 83 mg (approximately 5.6%) of a mixture of **23** and **24**. Elution with CH$_2$Cl$_2$ gave 221 mg (0.54 mmol, 13.1%) of **25** (fractions 33–40). Crystallization followed as above.

This experiment was repeated 3 times in all. Product distributions are summarized in Table I.

Rearrangements of [4,4′-^{13}C$_2$]**18** were carried out in the same way. Times for low conversions were 24, 32, and 38 min, while $[\mathbf{18}]_0$ was, correspondingly, 0.028, 0.02, and 0.02 M. Product distributions are summarized in Table I.

Rearrangements of [2-^{14}C]**18** and [4-^{14}C]**18** were carried out in the same way, except that initial concentrations were 0.019 M [2-^{14}C]**18** and 0.026 M [4-^{14}C]**18**. Each trifluoroacetylated product was sublimed once after three crystallizations and prior to scintillation counting. Only **23** and **24** were isolated in rearrangements of [2-^{14}C]**18**.

KIE Measurements. Whole-molecule-ion mass spectrometry (WMIMS) was carried out successfully in measuring isotopic abundances only in products **23** and **25** from rearrangements of [^{15}N,^{15}N′]**18**. Reproducible results could not be obtained by WMIMS for [^{15}N,^{15}N′]**24** and also for any of the derivatives of the ^{13}C-labeled products. Failure to obtain reproducible results with samples of **24** derived from the difficulty in controlling a steady concentration of **24** in the mass spectrometer, and this led to problems with the electron multiplier. Failure to obtain reproducible results with any ^{13}C-labeled sample derived, as was found later, from the absence of carbon KIE in the rearrangements, resulting in WMIMS measurements that were scattered widely around the error limits of the instrumentation.

WMIMS measurements were made with a Hewlett-Packard quadrupole mass spectrometer, Model 5995, operated in the selected-ion-monitoring mode. Samples were introduced via a direct insertion probe (DIP) and the source pressure was maintained at 3×10^{-7} torr by controlled heating of the sample. Samples of **23** were heated externally in a specially designed probe and bled into the source via needle valves. A total of 10000–29000 scans of relative abundances was made per sample and were analyzed statistically in 25 blocks; that is, for example, when 10000 scans were made each block of 400 scans was averaged and the 25 results were treated statistically. The method has been described earlier.[3,4]

Isotope-ratio mass spectrometry was carried out in the laboratory of the Krueger Geochron Co. Samples were converted directly into N$_2$ and CO$_2$ by Sofer's method,[19] and the gases were analyzed for ^{29}N$_2$/^{28}N$_2$ and ^{45}CO$_2$/^{44}CO$_2$ ratios in a triple-collector instrument after cryogenic separation. The method and treatment of the "del" data have been described earlier.[5]

KIE were calculated with eq 7, in which F is the extent of low conversion and R_p and R_0 the isotopic ratios at low and 100% conversion, respectively.[20]

$$k_L/k_H = \ln (1 - F)/ \ln (1 - R_pF/R_0) \qquad (7)$$

Scintillation counting was carried out with a Beckman Model LS7000 liquid scintillation counter. Four separate 5-mg samples of each derivative, weighed precisely on a Cahn balance to ±0.001 mg, were counted 7–11 times each. The average of counts per 1.000 mg was used in KIE calculations.

HPLC analysis: The mixture of the trifluoroacetyl derivatives of the products of rearrangement of unenriched **18** was dissolved in acetonitrile. Acetanilide was used as an internal standard. The flow solvent was 38% aqueous acetonitrile. Quantitative assays were made with a Varian integrating computer, Model CDS111, using response factors established with authentic samples. In the assay of **23** a calibration curve was also used as a check on response-factor data. Results are given in run 13, Table I.

Acknowledgment. This work was supported by the Robert A. Welch Foundation, Grant D-028, and the National Science Foundation, Grant CHE 8314947.

---

(19) Sofer, Z. *Anal. Chem.* **1980**, *52*, 1389.

(20) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley-Interscience: New York, 1980; p 100.

Photochemical Trans ⇌ Cis Isomerization of 1,2-Bis(heteroaryl)ethylenes: 1,2-Bis(pyrazinyl)ethylene

Pill-Hoon Bong,[†] Hyeong Jin Kim,[†] Kyu Ho Chae,[†‡] Sang Chul Shim,*[†] Nobuaki Nakashima,[§] and Keitaro Yoshihara[§]

Contribution from the Department of Chemistry, Korea Advanced Institute of Science and Technology, Cheongyangni, Seoul 131, Korea, and the Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

Received December 13, 1984

Abstract: The direct and sensitized trans ⇌ cis photoisomerization of 1,2-bis(pyrazinyl)ethylene is investigated in various conditions. Quantum yields of the direct trans → cis photoisomerization increase with increasing solvent polarity because of the proximity of the lowest $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states. Azulene quenches the direct and sensitized photoisomerization, giving the same Stern–Volmer constant indicating that the triplet state is the reactive state in both cases. The directly measured triplet lifetime of *trans*-1,2-bis(pyrazinyl)ethylene by laser spectroscopy is the same as the lifetime calculated from the azulene quenching studies. Laser spectroscopy also indicates efficient intersystem crossing following direct irradiation. From these results, it is concluded that the direct photoisomerization of 1,2-bis(pyrazinyl)ethylene proceeds through the triplet manifold in contrast to stilbene which undergoes direct trans ⇌ cis photoisomerization through the singlet manifold.

The photochemical behavior of stilbene has been studied extensively, and the photoreaction mechanism is well-understood.[1-3] Experimental observations have established that the unsubstituted stilbene isomerizes in the singlet manifold.[1,4] The photochemical reactions and spectroscopy of nitrogen heterocyclic compounds have also been the subject of considerable investigation and

---

[†] Korea Advanced Institute of Science and Technology.

[‡] Department of Polymer Engineering, College of Engineering, Chonnam National University, Kwang Ju 505, Korea.

[§] Institute for Molecular Science.

(1) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. *Org. Photochem.* **1973**, *3*, 1 and references therein.

(2) (a) Orlandi, G.; Siebrand, W. *Chem. Phys. Lett.* **1975**, *30*, 352. (b) Orlandi, G.; Palmieri, P.; Poggi, G. *J. Am. Chem. Soc.* **1979**, *101*, 3492. (c) Orlandi, G.; Marconi, G. *Nuovo Cimento* **1981**, *63B*, 332.

0002-7863/86/1508-1006\$01.50/0

Table I. Quantum Yields for the Direct and Biacetyl-Sensitized Photoisomerization of BPyE in Various Solvents at Different Irradiation Wavelengths

solvents	at 313 nm		at 366 nm		at 435.8 nm[c]		
	Φ_c[a]	Φ_t[b]	Φ_c[a]	Φ_t[a]	Φ_c[a]	Φ_t[a]	Φ_{isc}[d]
benzene	0.086	0.009	0.229	0.036	0.406	0.474	0.564
PhH–CH_2Cl_2[e]	0.089		0.219		0.430	0.520	0.509
CH_2Cl_2	0.117	0.014	0.260	0.054	0.430	0.528	0.605
bromobenzene			0.260	0.080			0.605
t-BuOH			0.280				0.651
ethanol	0.057	0.011	0.307	0.051	0.430	0.560	0.714
CH_3CN–H_2O[f]	0.067	0.010	0.351	0.051	0.430	0.560	0.816
methanol			0.424				0.986

[a] Concentrations of *trans*- and *cis*-BPyE are 2.5×10^{-3} M. [b] Concentration of *cis*-BPyE is 1.0×10^{-3} M. [c] Biacetyl-sensitized isomerization quantum yields (concentration of biacetyl is 0.25 M, absorbance $\simeq$ 2.0). [d] Quantum yields of intersystem crossing of *trans*-BPyE calculated by (1). [e] 50% CH_2Cl_2 by volume. [f] 70% CH_3CN by volume.

controversy.[5-7] The introduction of nitrogen atoms into the phenyl rings significantly affects the photophysical and photochemical behavior of stilbene because of the involvement of the (n,π^*) state in the reaction mechanism. The proximity of the (n,π^*) state to the lowest (π,π^*) state in pyridine enhances radiationless transitions (mainly internal conversion, $^1S \rightsquigarrow {}^0S$, $\Phi_{ic} \simeq 1.0$), while intersystem crossing is tremendously enhanced in pyrazine ($\Phi_{isc} \simeq 1.0$, $\Phi_{ph} \simeq 1.0$) compared to benzene ($\Phi_{isc} \simeq 0.25$, $\Phi_f \simeq 0.05$).[8,9]

The stilbazoles, styrylpyridines (StP's), and 1,2-dipyridylethylenes (DEP's) have been studied extensively by Whitten et al.[5,6] and Mazzucato et al.[10,11] They found a reasonably efficient benzophenone-sensitized photoisomerization in DPE's, while direct photoisomerization was very inefficient compared to stilbazoles and StP's. Based on theoretical considerations, El-Sayed[8a] concluded that intersystem crossing in diazines, such as pyrazine, proceeds much more rapidly than the other transitions. However, internal conversion is shown to be an important process for 2-stilbazole and all the DPE's. Therefore, the results of DPE's as with stilbene indicate that the intersystem crossing does not occur efficiently on direct irradiation, and its isomerization occurs through the singlet manifold.

The 1,2-bis(pyrazinyl)ethylene (BPyE) is a tetraazastilbene which has both (n,π^*) and (π,π^*) excited states in contrast to stilbenes. The replacement of phenyl rings with pyrazine should therefore enrich the photochemistry of the stilbene to a considerable extent. In this system, the $^1(n,\pi^*)$ state has about the same energy as the $^1(\pi,\pi^*)$ state, and consequently extensive mixing between these two states results in obscuring the $^1(n,\pi^*)$ band.[12] In this investigation, the direct and sensitized trans ⇌ cis photoisomerization of BPyE is studied under a variety of conditions. The experimental results are compared with those of the stilbenes, azastilbenes, and diazastilbenes.

Experimental Section

Materials. Extra pure solvents were used as received or after distillation. *trans*-1,2-Bis(pyrazinyl)ethylene (BPyE), prepared by the reported method[12] starting from pyrazinecarboxylic acid, was recrystallized from acetone. *cis*-BPyE was prepared from *trans*-BPyE by photochemical reaction. *trans*-BPyE was dissolved in benzene, and the solution was degassed by bubbling with nitrogen gas for 1 h and irradiated with UV light (350 nm) in a Rayonet photochemical reactor for 2 h. *cis*-BPyE was isolated by column chromatography on silica gel (70–230 mesh, ethyl acetate/acetone/chloroform; 15/6/5, v/v) and recrystallized from cyclohexane. Benzophenone was received from Sigma Chemical Co. and recrystallized from cyclohexane. Biacetyl (Aldrich) was used without further purification, and azulene (Aldrich) was purified by vacuum sublimation.

Spectra. Absorption spectra were recorded on a Cary 17 spectrophotometer. Emission spectra were recorded on an Aminco Bowman spectrophotofluorometer with Aminco *XY* recorder. High-performance liquid chromatogram was obtained on a Waters Assoc. Model 244 equipped with Model 6000A solvent delivery system and Model 440 absorbance detector (254 and 280 nm).

Quantum Yield Measurements. Samples for quantum yield determination were degassed and sealed in Pyrex ampules. Usually, 3 mL of sample solution was pipetted into the ampules, degassed through three to five freeze–pump–thaw cycles with cooling in liquid nitrogen, and sealed. The solutions in the sealed ampules were irradiated with a Hanovia 450 W medium-pressure mercury arc lamp (Type 697A36) in a merry-go-round apparatus. Mercury emission lines of 313.0, 366.0, and 435.8 nm were isolated by filters for the direct and sensitized photoisomerization. The following filters were used: 313.0 nm, No. 7–54 Corning glass filter and 0.7-cm path of 0.0025 M K_2CrO_4 in 1% Na_2CO_3 aqueous solution; 366.0 nm, Corning glass filters No. 0–52 and 7–37; 435.8 nm, 7.5 g of $NaNO_2$ in 100 mL of aqueous solution and 0.44 g of $CuSO_4 \cdot 5H_2O$ in 100 mL of 2.7 M NH_4OH aqueous solution. Ferrioxalate actinometry was used to monitor the intensity of the exciting light.[13] Quantitative analyses were carried out by HPLC techniques. The conditions of HPLC quantitation are shown below. Quantum yields of isomerization were determined by using low conversions (1–5%) to prevent appreciable back-reaction.

sample solvent	column and phase	quantitation method	eluting solvents
nonpolar	μ-Bondapak CN (3.9 mm i.d. × 30 cm), normal	peak height	*n*-hexane/ethyl ether/acetonitrile (v/v, 11/3/1) or *n*-hexane/ethyl ether/methanol (v/v, 100/10/1)
polar	μ-Bondapak C_{18} (3.9 mm i.d. × 30 cm), reverse	peak area or height	water/methanol/tetrahydrofuran (v/v, 40/40/3)

Laser Flash Photolysis. The nanosecond laser photolysis apparatus has been described elsewhere.[43] The laser flash photolysis experiments were carried out by using a XeF (351 nm) and a KrF (248 nm) excimer laser (Lambda Physik EMG101E) as excitation light sources. The concentrations (1.0–2.0×10^{-5} M) of *trans*- and *cis*-BPyE were adjusted such that suitable amounts of the laser light were absorbed. The lifetimes for decay of the transient and ground-state *trans*-BPyE depletion were directly obtained from oscillograms.

Results and Discussion

Direct Photoisomerization. Quantum yields for the direct and sensitized photoisomerization of BPyE in several solvents and at

---

(3) (a) Birch, D. J. S.; Birks, J. B. *Chem. Phys. Lett.* **1976**, *38*, 432. (b) Birks, J. B.; *Ibid.* **1976**, *38*, 437.

(4) Saltiel, J.; Marinari, A.; Chang, D. W.-L.; Mitchener, J. C.; Megarity, E. D. *J. Am. Chem. Soc.* **1979**, *101*, 2982.

(5) Whitten, D. G.; McCall, M. T. *J. Am. Chem. Soc.* **1969**, *91*, 5097.

(6) Lee, Y. J.; Whitten, D. G.; Perderson, L. *J. Am. Chem. Soc.* **1971**, *93*, 6330.

(7) Whitten, D. G.; Lee, Y. J. *J. Am. Chem. Soc.* **1972**, *94*, 9142.

(8) (a) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834. (b) Lower, S. K.; El-Sayed, M. A. *Chem. Rev.* **1966**, *66*, 199.

(9) (a) Kasha, M. *Discuss. Faraday Soc.* **1959**, *9*, 14. (b) Goodman, L. *J. Mol. Spectrosc.* **1961**, *6*, 109.

(10) Bortolus, P.; Favaro, G.; Mazzucato, U. *Mol. Photochem.* **1970**, *2*, 311.

(11) Mazzucato, U. *Pure Appl. Chem.* **1982**, *54*, 1705 and references therein.

(12) Shim, S. C.; Lee, D. S.; Chae, J. S.; Song, P.-S. *Taehan Hwahakhoe Chi*, **1976**, *20*, 398.

(13) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* *A235*, 518.

different wavelengths of the exciting light are summarized in Table I. The quantum yields of the direct photoisomerization at 313 nm are smaller than those at 366 nm and decrease as the viscosity of solvents increases. A similar wavelength effect was observed by Zimmerman et al.[14a] with regard to the quantum yields of trans → cis isomerization of azobenzene at different wavelengths of exciting light. If the higher excited electronic levels are deactivated thermally to the first excited level very fast, one would expect the quantum yield to be independent of the wavelength, if not higher at shorter wavelengths. However, the trans→cis quantum yields observed in azo compounds,[14] such as azobenzene, are lower for light absorbed at the shorter wavelength within the two bands in the UV absorption. In certain cases, this wavelength effect was attributed to competitive radiationless transitions from such higher levels to the ground state, directly violating Kasha's rule. Such a wavelength effect was also reported by Mazzucato et al. in the photoisomerization of styrylpyridines,[15] and the same rationale can be applied to the present results.

The quantum yields of the direct trans → cis photoisomerization of unsubstituted stilbene[16] and 4,4′-dinitrostilbene[17] are not affected by solvent polarity but are affected by solvent viscosity. However, the quantum yields of the direct photoisomerization of BPyE at 366 nm are strongly affected by solvent polarity (Table I). The photocyclization quantum yields of *cis*-BPyE and the photoreduction of *trans*-BPyE are similarly affected by solvent polarity.[18]

cis-BPyE isomerizes to *trans*-BPyE with efficiencies much lower than that of trans→cis isomerization as observed in simple stilbenes.[19b] For example, the quantum yield of cis → trans isomerization in benzene at 366 nm is 0.036, but the quantum yield of trans → cis isomerization is 0.23. In the earlier studies for stilbene,[19] decay from the cisoid excited singlet, $^1c^*$, was found to be practically temperature-independent and to lead almost exclusively to the state from which isomerization takes place. A marked drop in the quantum yield of cis → trans isomerization at low temperatures was due mainly to increased medium rigidity and not to an internal barrier to rotation. The similar values of $\Phi_t = 0.474$ and $\Phi_c = 0.406$ for the biacetyl-sensitized isomerization of BPyE in benzene (Table I) suggests efficient formation of $^3p^*$ from both $^3t^*$ and $^3c^*$. The suggestion that enhanced spin–orbit coupling induces very rapid $^1c^* \rightarrow {}^3c^* \rightarrow {}^1c$ decay,[20,21] accounting for a decrease in Φ_t for the direct excitation photoisomerization, can therefore be discounted. The major deactivation pathways of the nonfluorescent excited *cis*-BPyE are two competitive processes, cis → trans isomerization and cis → DHP conversion (DHP = 4a,4b-dihydrophenanthrene derivative, the photocyclization product). Under deoxygenated conditions, however, photochemical cis ⇌ trans isomerization of BPyE takes place with essentially no net loss in the total amount of BPyE. It suggests that the DHP must undergo ring opening with unit efficiency under the irradiation conditions to regenerate *cis*-BPyE. It is then obvious why the quantum yields of cis → trans isomerization are smaller than those of trans → cis isomerization on direct irradiation.

The data in Table I indicate that deactivation of the singlet state of BPyE must include radiationless decay processes which proceed by paths not involving trans ⇌ cis isomerization (the fluorescence quantum yield of *trans*-BPyE, Φ_{fl}, is 0.025 for 366-nm excitation and 0.015 for 313-nm excitation in EPA at 77 K, and is 0.003 in benzene at room temperature for 366-nm excitation; no phosphorescence was observed even at 77 K).[12,22] An obvious possibility for explaining the rapid rates of radiationless decay in BPyE is the involvement of an (n, π^*) state. There is increasing evidence that aza aromatics with the lowest lying (n, π^*) state have rapid rates of internal conversion. From studies of several aza aromatics, Hochstrasser and Marzzacco[23] have concluded that compounds which have either the lowest (n, π^*) state or (π, π^*) state where (n, π^*)–(π, π^*) mixing occurs show enhanced radiationless transition rates. The enhancement of radiationless decay on introduction of the second nitrogen atom into stilbene can be explained on the same basis. If (n, π^*)–(π, π^*) mixing or some other phenomena involving (n, π^*) states is to account for the different results in quantum yields of direct photoisomerization and intersystem crossing between 3-stilbazole and 3,3′-DPE and between 4-stilbazole and 4,4′-DPE, Whitten and McCall[5] concluded that there is considerable interaction of cooperation between nitrogens in the DPE's. Both experimental and theoretical studies[25,26] have established that the (n, π^*) transitions in pyrazine are separated much more (as much as 1 eV or more) than was originally suspected[24] (ca. 400 cm^{-1}) and that the fall off of this energy gap is sharp as the nitrogen separation increases from pyridazine to pyrazine.

Table II. Effect of Benzophenone on the Sensitized Trans → Cis Photoisomerization of BPyE[a] at 366 nm

benzophenone concn M	A/A_0[b]	Φ_c[c]	Φ_c[d]	Φ_c[e]	Φ_c[f]
0	1.00	0.229	0.219	0.260	0.351
5.0×10^{-3}	0.90	0.231	0.197		0.323
1.0×10^{-2}	0.82	0.226	0.176	0.220	0.286
2.5×10^{-2}	0.65				0.251
5.0×10^{-2}	0.48	0.179	0.114		
1.0×10^{-1}	0.32	0.143	0.085	0.216	
2.5×10^{-1}	0.16	0.089	0.076	0.043	

[a] Concentration of *trans*-BPyE is 2.5×10^{-3} M. [b] A/A_0 is the fractions of photons absorbed by BPyE in this condition. [c] In benzene. [d] In benzene–dichloromethane (v/v, 1:1). [e] In dichloromethane. [f] In acetonitrile–water (v/v, 7:3).

As the solvent polarity increases, intersystem crossing in *trans*-BPyE is enhanced because the $^1(\pi, \pi^*)$ state and lowest $^1(n, \pi^*)$ state are mixed extensively both by increasing the energy of the $^1(n, \pi^*)$ state and by decreasing the energy of the $^1(\pi, \pi^*)$ state. In our previous paper,[18] we reported that the quantum yields of photoreduction and photocyclization from the $^1(n,\pi^*)$ state of *trans*-BPyE and *cis*-BPyE decrease sharply as the polarity of the solvents is increased because of the same reasons.

Sensitized Photoisomerization. When solutions of stilbenes are directly irradiated, diverse reactions such as isomerization, reduction, dimerization, cyclization, and fluorescence are observed,[5,27] whereas only trans ⇌ cis isomerization has been detected in triplet-sensitized reactions.

Quantum yields of benzophenone-sensitized photoisomerization of BPyE in several solvents at 366 nm are summarized in Table II. The fractions of photons absorbed by BPyE under these conditions are also shown. The observed quantum yields of trans → cis isomerization are larger than calculated values for the fractions of directly excited BPyE ($\Phi_c^{cal} = \Phi_c^0 \times A/A_0$, where Φ_c^0 is the quantum yield of direct trans → cis photoisomerization). It indicates that the observed quantum yields are the sum of the direct and triplet-sensitized photoisomerization quantum yields. However, the quantum yields of trans → cis isomerization by benzophenone sensitization decrease as the concentration of benzophenone increases, indicating that all the benzophenone triplets do not generate effectively the olefin triplets. This phenomenon can be observed when the energy transfer from the sensitizer triplet to the triplet of BPyE is inefficient or when

---

(14) (a) Zimmerman, G.; Chow, L.-Y.; Paik, U.-J. *J. Am. Chem. Soc.* **1958**, *80*, 3528. (b) Fischer, E. *Ibid.* **1960**, *82*, 3249. (c) Malkin, S.; Fischer, E. *J. Phys. Chem.* **1962**, *66*, 2482. (d) Weker, G.; Teale, F. W. J. *Trans. Faraday Soc.* **1958**, *54*, 640.

(15) Bartocci, G.; Mazzucato, U. *J. Luminsc.* **1982**, *27*, 163.

(16) Schulte-Frohlinde, D. *Liebigs Ann. Chem.* **1958**, *612*, 138.

(17) Schulte-Frohlinde, D.; Blume, H.; Güsten, H. *J. Phys. Chem.* **1962**, *66*, 2486.

(18) Shim, S. C.; Lee, S. K. *Bull. Korean Chem. Soc.* **1980**, *1*, 68.

(19) (a) Malkin, S.; Fischer, E. *J. Phys. Chem.* **1964**, *68*, 1153. (b) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 12. (c) Sharafy, S.; Muszkat, K. A. *Ibid.* **1971**, *93*, 4119.

(20) Krüeger, K.; Lippert, E. *Z. Phys. Chem.* **1969**, *66*, 293.

(21) (a) Lippert, E. *J. Phys. Chem.* **1964**, *42*, 125. (b) Lippert, E. *Acc. Chem. Res.* **1970**, *3*, 74.

(22) Shim, S. C.; Cho, J. H. *Taehan Hwakakhoe Chi* **1979**, *23*, 325.

(23) Hochstrasser, R. M.; Marzzacco, C. *J. Chem. Phys.* **1967**, *46*, 4155.

(24) (a) El-Sayed, M. A.; Robinson, G. W. *Mol. Phys.* **1961**, *4*, 273. (b) El-Sayed, M. A.; Robinson, G. W. *J. Chem. Phys.* **1961**, *34*, 1840.

(25) Hoffman, R. *J. Chem. Phys.* **1964**, *40*, 2745.

(26) Clementi, E. *J. Chem. Phys.* **1967**, *46*, 4731 and 4737.

(27) Whitten, D. G.; Lee, Y. J. *J. Am. Chem. Soc.* **1970**, *92*, 415.

Table III. Quantum Yields for Biacetyl Sensitized Trans → Cis Photoisomerization of BPyE, Stilbene, StP's, and DPE's in Benzene at 435.8 nm

acceptor	Φ_c^{dir}	Φ_c^{sens}	$\Phi_c^{dir}/\Phi_c^{sens}(\Phi_{isc})^a$	$\Phi_{isc}^{obsd\,b}$
stilbene[c]	0.43	0.4		negligible
2-StP[c]	0.22	0.46	0.48	negligible
3-StP[c]	0.52	0.54	0.96	negligible
4-StP[c]	0.37	0.48	0.77	negligible
2,2′-DPE[c]	0.01	0.13	0.08	negligible
3,3′-DPE[c]	0.08	0.48	0.17	negligible
4,4′-DPE[c]	0.003	0.45	0.007	negligible
t-BPyE[d]	0.23	0.41	0.56_4	0.56_4[e]

[a] Calculated by using (1). [b] From the results observed by pulse radiolysis and laser flash photolysis (ref 31). [c] From ref 5 and 10. [d] Our experimental results in benzene. [e] Our experimental results in *n*-hexane by laser flash photolysis.

benzophenone triplets are quenched through self-quenching or by the triplet–triplet annihilations. It is very likely that benzophenone triplet self-quenching is the major factor.

Quantum yields for biacetyl-sensitized isomerization of BPyE in several solvents at 435.8 nm are summarized in Table I. BPyE undergoes fairly efficient geometrical isomerization when photosensitized by biacetyl in contrast to the sensitized photoisomerization by benzophenone. The quantum yields of intersystem crossing were calculated by using the following equation assuming that photoisomerization occurs on the triplet surface. In nonpolar solvents,

$$\Phi_{isc} = \Phi_{direct}^{at\ 366\ nm} / \Phi_{biacetyl\ sensitized}^{at\ 435.8\ nm} \qquad (1)$$

the higher trans → cis quantum yields in the biacetyl-sensitized photoisomerization than in the direct photoisomerization indicate that the excited singlet states do not exclusively decay to the triplet state on direct irradiation or that isomerization occurs on the singlet surface less efficiently than on triplet surface.

Quantum yields of the biacetyl-sensitized trans → cis isomerization of stilbene, StP's, and DPE's are also reported in Table III together with the data of the direct photoisomerization for comparison. Differences in the quantum yields for the sensitized reaction of the isomeric StP's and DPE's are small, indicating a similar reactivity of the triplet acceptors, practically independent of the nitrogen positional isomerism in contrast to the fluorescence[5,7,28,29] and the photocyclization reaction.[20] A significant quantum yield decrease was however observed for the 2,2′-DPE contrary to StP's and other DPE's.

Photophysical and Photochemical Properties. In order to determine the effect of the introduction of (n, π*) states, photophysical and photochemical properties of BPyE were investigated and compared with those of stilbene, StP's, and DPE's as summarized in Table IV. BPyE in an inert solvent at room temperature shows Φ_{fl} and Φ_{nr} values between those of ortho (2-StP and 2,2′-DPE) and meta (3-StP and 3,3′-DPE) azastilbenes. This is due to the position of the nitrogen atoms, the same ortho and meta positions in BPyE as in 2-StP and 2,2′-DPE, and 3-StP and 3,3′-DPE. The fluorescence quantum yields of BPyE at low temperature, however, do not increase to near unity at 77 K but are far smaller than unity. It appears from Table I that the internal conversion probably is a negligible process for BPyE whilst efficient intersystem crossing is operative in polar solvents.

Theoretical calculations[28,30] predict that intersystem crossing occurs at a much faster rate in 2- and 4-StP compared with stilbene and 3-StP because of lower thermal barrier exerted by π and π* orbitals which have nodes in the meta positions. The intersystem crossing, however, is not fast enough to compete with the fast internal rotation ($^1t^* \rightarrow {}^1p^*$) or internal conversion ($^1t^* \rightarrow {}^1t$) at room temperature in fluid solutions and is almost negligible in fluid solvents as confirmed by pulse radiolysis and laser flash photolysis experiments, which indicated a triplet yield approaching undetectable limits.[31] The major fractions of the excited singlet states of StP's are deactivated by the net internal conversion process in contrast to BPyE. In StP's, the internal conversion probably makes an important contribution at room temperature, and intersystem crossing becomes important only when the photoisomerization rate in an inert solvent is negligible (at low temperature). The reduction of nonradiative decay at low temperature leads to an increase in Φ_{fl} at 77 K, as observed in the EPA matrix (Table IV). The increase in energy of the (n,π*) state in polar media also lowers the efficiency of both radiationless unreactive processes (internal conversion and intersystem crossing). The internal conversion also seems to be the major decay path for DPE's, especially when the nitrogen atoms are in the ortho or para positions. Theory predicts that in the three symmetrical isomers, the lowest excited singlet state is ethylenic and the (n,π*) states lie at least 0.3 eV above it and that there is a strong mixing between ^{1}S and the pyridinic states located nearby.[28] This produces an efficient internal conversion to ^{0}S. The spin–orbit coupling has been evaluated and leads to intersystem crossing rate parameters not far from those of StP's, here again the lowest value being that of the meta compound.[28] As in the case of stilbene and StP's, intersystem crossing of DPE's also becomes operative in a rigid matrix at low temperature when the isomerization does not occur.

In contrast to these results of StP's and DPE's, intersystem crossing of BPyE is important at room temperature, and the increase in energy of the ^{1}(n,π*) state in polar media increases the quantum yields of intersystem crossing. The fluorescence efficiency of BPyE at 77 K differs from those of StP's and DPE's. The triplet formation in BPyE is also observed by laser flash photolysis at room temperature in contrast to DPE.

The reported quantum yields of the direct photoisomerization of azastilbenes with the exception of 2-StP and DPE's are not far from those of the sensitized processes. The intersystem crossing efficiencies of the acceptors (stilbene, 3-StP, and 4-StP) calculated by (1) are much larger than those of 2-StP and DPE's (Table III). The intersystem crossing of these compounds (stilbene and their aza analogues) is, however, reported to be almost negligible in solution at room temperature.[31] The higher quantum yields of trans → cis isomerization, always found in the sensitized reactions, indicate that the excited singlet state does not exclusively decay to the triplet state.

The reported quantum yields of the direct photoisomerization of the three isomers of DPE's are much smaller than those of stilbene and all the StP's. The low quantum yields are explained as mainly resulting from a scarce population of the triplet state by intersystem crossing and not from radiationless decay of the triplet state. The major fraction of the excited singlet states in DPE's is deactivated by net internal conversion, and intersystem crossing is almost negligible in fluid solutions. The quantum yields of the trans → cis isomerization of BPyE on direct irradiation, however, are similar to those of 2-StP, and the sensitized photoisomerization quantum yields are similar to those of stilbene and their aza analogues. These results are attributed to the efficient intersystem crossing process of singlet state and suggest that the trans → cis photoisomerization proceeds via the triplet state to StP's and DPE's. Therefore, the mechanism of direct trans ⇌ cis photoisomerization of BPyE may differ from that of StP's and DPE's.

Quenching Studies by Azulene. The quenching of the excited states of stilbenes and their aza analogues by azulene has been studied extensively.[1,4,7,32,33] It is found that azulene quenches the

---

(28) (a) Orlandi, G.; Poggi, G.; Marconi, G. *J. Chem. Soc. Faraday Trans. 2* **1980**, *76*, 598. (b) Bartocci, G.; Mazzucato, U.; Masetti, F.; Galiazzo, G. *J. Phys. Chem.* **1980**, *84*, 847.

(29) Bartocci, G.; Bortolus, P.; Mazzucato, U. *J. Phys. Chem.* **1973**, *77*, 605.

(30) (a) Gregory, A. R.; Siebrand, W.; Williams, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 1903. (b) Distefano, G.; Mazzucato, U.; Modelli, A.; Pignataro, S.; Orlandi, G. *J. Chem. Soc., Faraday Trans.* **1975**, 1583.

(31) Bensasson, R. V.; Land, E. J., private communication.

(32) (a) Saltiel, J.; Megarity, E. D.; Kneipp, K. G. *J. Am. Chem. Soc.* **1966**, *88*, 2336. (b) Saltiel, J.; Megarity, E. D. *Ibid.* **1969**, *91*, 1265. (c) Saltiel, J.; Megarity, E. D. *Ibid.* **1972**, *94*, 2742. (d) Saltiel, J.; Chang, D. W. L.; Megarity, E. D.; Rousseau, A. D.; Shannon, P. T.; Thomas, B.; Uriarte, A. K. *Pure Appl. Chem.* **1975**, *41*, 559.

Table IV. Photophysical and Photochemical Parameters of *trans*-BPyE in *n*-Hexane (at Room Temperature) and in EPA (at 77 K)

	in *n*-hexane (at room temp)[a]				in EPA (at 77 K)[b]		
compounds	Φ_{fl}	τ_{fl}^{cal}, ns	k_{fl}, 10^8 s^{-1}	Φ_{nr}	Φ_{fl}^{lim}	τ_{fl}^{lim}, ns	k_{fl}^{lim}, 10^8 s^{-1}
stilbene	0.036	0.09	4	0.964	1.00	1.5	6.7
2-StP	0.0008	0.007	1.1	0.999	1.00	1.0	10
3-StP	0.075	0.19	4	0.925	0.92	1.5	6.1
4-StP	0.0016	0.008	2	0.998	0.87	1.0	8.7
2,2′-DPE[c]	0.005	0.16	3.1	0.995			
3,3′-DPE[c]	0.13	0.39	3.3	0.87			
4,4′-DPE[c]	0.0004	0.0009	4.7	0.999_5			
t-BPyE	0.003[d]	0.28	0.1	0.997	0.025	0.58	0.43

[a] From ref 28a and 29. [b] From ref 28b. [c] From ref 5 and 7. [d] Our experimental results in benzene (at room temperature).

Table V. Azulene Effect on the Direct and Sensitized Photoisomerization of BPyE

	on the direct			on the sensitized		
compounds	intercept	slope/intercept, M^{-1}	$1/k_d$,[g] ns	intercept	slope/intercept, M^{-1}	$1/k_d$,[g] ns
stilbene[a]	0.17	14.0, 22		0.69	53	
3,3′-DPE[b]		90			250	
4,4′-DPE[b]		70			280	
3-StQ[c]	0.75	165		0.90	150	
BPyE[d]	0.01_5[f]	1.4×10^3	160	1.19 (1.21)[f]	1.4×10^3	160
		1.1×10^3[e]	160		1.1×10^3[e]	160

[a] From ref 32b (in benzene). [b] From ref 6 and 7 (in *t*-BuOH). [c] From ref 34. [d] Our experimental results in benzene–dichloromethane (v/v, 1:1). [e] In acetonitrile–water (v/v, 7:3). [f] Intercept calculated from Table I ($\epsilon_{trans}/\epsilon_{cis} \simeq 4$ at 366 nm). [g] $1/k_d$ is calculated by assumption $k_{az} \simeq k_{diff} = 8RT/3750\eta$ (then, η is the viscosity of solvent and calculated by fraction of volume, ref 32d).

excited trans triplet states, $^3t^*$, of stilbene which has a finite lifetime but does not affect short-lived cis triplet states, $^3c^*$, in the sensitized photoisomerization. Assuming the selective quenching of the transoid excited state by azulene and using the steady-state approximation on the excited species, the following Stern-Volmer relationship can be derived

$$\Phi_c^0/\Phi_c = 1 + k_q\tau[\mathrm{Az}] \qquad (2)$$

where, k_q is the quenching rate constant which is assumed to be the same as the diffusion-controlled rate constant, τ is the lifetime of quenched species, and Φ_c^0 is the quantum yield of trans → cis isomerization in the absence of azulene.

Azulene quenching of the direct and sensitized trans → cis isomerization of BPyE can be conveniently assessed by measuring initial isomerization efficiencies. The data on the azulene effect on direct and sensitized isomerization yields give good linear Stern–Volmer plots (Figure 1), showing the slopes of 1.4×10^3 M^{-1} in benzene–dichloromethane (v/v, 1:1) and 1.1×10^3 M^{-1} in acetonitrile–water (v/v, 7:3), respectively. Interestingly BPyE shows a much bigger slope/intercept ratio compared to 14.0 M^{-1} (in direct isomerization) and 53 M^{-1} (in sensitized isomerization) for stilbene in the plot of [trans]/[cis] ratios at the photostationary state vs. [azulene].[32b,c]

Since the concentration of azulene was kept low and molar absorption coefficients of *trans*-BPyE ($\epsilon \sim 4 \times 10^3$, 2.5 mM) and sensitizer ($\epsilon \sim 60$, 0.025–0.5 M) are much larger than that of azulene ($\epsilon \sim 10$, 1–5 mM) at the wavelength used (366 nm), the absorption of light by azulene itself is negligible.

The excited singlet state of *trans*-BPyE can be quenched by azulene in direct irradiation. The fluorescence quenching by azulene, however, was inefficient, showing the fluorescence quenching constant of lower than 9.0×10^7 M^{-1} s^{-1} in the Stern–Volmer plot. Since the intersystem crossing rate constant was determined to be ca. 3.5×10^9 s^{-1} and Φ_F is very low (0.003), the singlet quenching of *trans*-BPyE by azulene is negligible in our experimental conditions.

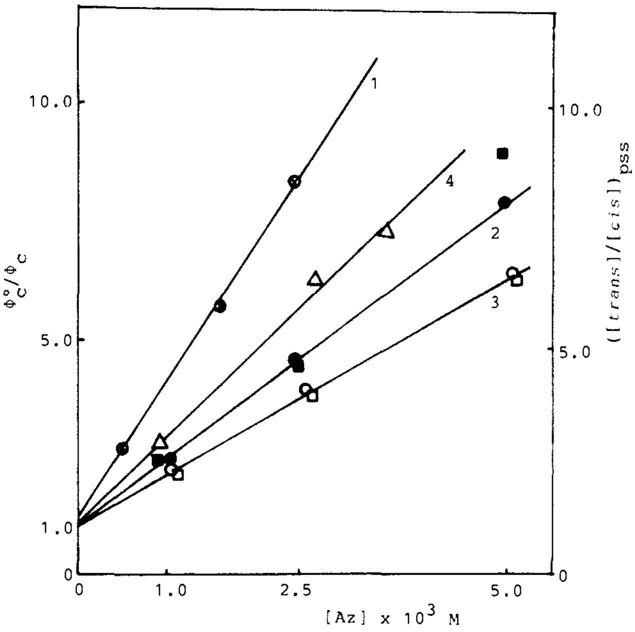


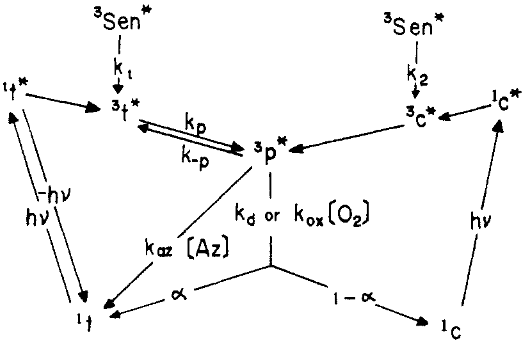
Figure 1. Effect of azulene quenching on the direct and sensitized photoisomerization of 1,2-bis(pyrazinyl)ethylene; line 1, the biacetyl-sensitized photostationary state ($[\mathrm{trans}]/[\mathrm{cis}])_{pss}$ ratio (⊗); line 2, the Stern–Volmer plot on the direct (●) and the biacetyl-sensitized (■) trans → cis photoisomerization in benzene–dichloromethane (v/v, 1:1); line 3, the Stern–Volmer plot on the direct (○) and the benzophenone (0.025 M) sensitized trans → cis photoisomerization (□) in acetonitrile–water (v/v, 7:3); line 4, benzophenone (0.5 M) sensitized (△).

As shown by Saltiel and Megarity,[32c] if a triplet mechanism is operative in both the direct and sensitized photoisomerization, identical slope/intercept ratios are expected in plots of the photostationary composition vs. [azulene], provided the fluorescence quenching of the trans excited singlet states by azulene is negligible which is the case. For the stilbene and DPE's, the slope of the Stern–Volmer plot in the azulene quenching is different between the direct and sensitized isomerization (Table V). Examination of all the kinetic possibilities for isomerization[32a] indicates the linear plots of (2) for the direct photoisomerization with a smaller slope than the value obtained for the singlet path only. Contrary to these results of stilbene and DPE's, azulene quenching studies by Gennari et al.[34] indicate that the trans →

---

(33) (a) Sumitani, M.; Yoshihara, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2503. (b) Saltiel, J.; Charlton, J. L. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980, Vol. 3, pp 25–89. (c) Saltiel, J.; Rousseau, A. D.; Thomas, B. *J. Am. Chem. Soc.* **1983**, *105*, 7631. (d) Görner, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1981**, *85*, 1835. (e) Saltiel, J.; Marchand, G. R.; Kirkor-Kaminska, E.; Smothers, W. K.; Mueller, W. B.; Charlton, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 3144.

Scheme I. Mechanism of the Photoisomerization of BPyE (Triplet Decay) and Interaction with Quenchers, where $^3p^*$ Is the Twisted (Phantom) Triplet Excited State



cis photoisomerization induced by direct irradiation of 3-styrylquinoline (3-StQ) proceeds via the triplet manifold.

As shown in Table V and Figure 1, azulene quenches the direct and triplet-sensitized trans → cis photoisomerization very efficiently, giving the same slope in the Stern–Volmer plot, and the slope is dependent on the viscosity of solvents. In triplet-sensitized isomerization, azulene competes with *trans*-BPyE for the sensitizer (benzophenone) triplets. When the concentration of benzophenone was lower than 0.025 M, *trans*-BPyE absorbed more than half of the light and *trans*-BPyE triplet states can be formed directly from the excited singlet state of *trans*-BPyE and also by energy transfer from the benzophenone triplets. Azulene can quench both benzophenone and *trans*-BPyE triplets. However, the same slope is obtained in the Stern–Volmer plots for direct and sensitized photoisomerization of *trans*-BPyE. This suggests very efficient triplet formation in direct irradiation of *trans*-BPyE. If the intersystem crossing to the triplet state is low in direct excitation of *trans*-BPyE, different slopes are expected in the Stern–Volmer plots for direct and benzophenone-sensitized photoisomerization of *trans*-BPyE. When benzophenone concentration is increased (>0.5 M), azulene will quench mostly benzophenone triplets, and bigger Stern–Volmer constants were obtained in the sensitized isomerization.

The slope/intercept ratio times α (the fraction of $^3p^*$ that decays to ^1t (Scheme I)), obtained from the linear plots of the photostationary state composition vs. [azulene] is same as the slope ($k_q\tau$) of the Stern–Volmer equation. The value of α can be obtained from the biacetyl-sensitized photoisomerization in methanol (Table I) in which Φ_c and Φ_t are observed to be 0.43 and 0.56, respectively. The $\Phi_c + \Phi_t$ value is near unity, and α is calculated to be 0.56. In the earlier studies, the slope of azulene quenching on the direct photoisomerization of stilbenes (singlet manifold photoisomerization) was found to be independent of the viscosity of solvents, whereas there is a sizable increase in the slope on the sensitized photoisomerization (triplet manifold photoisomerization) as the viscosity of solvents is decreased. These results of BPyE, therefore, suggest that the same excited triplet state is involved both in direct and triplet-sensitized photoisomerization which is similar to 3-StQ and in contrast to stilbene and DPE's.

The simplest mechanism which will account for these observations is shown in Scheme I. It should be noted that leaving out $^3t^*$ quenching by oxygen implies that $^3p^*$ is the thermodynamically favored geometry of BPyE triplets under the experimental conditions. A mechanism in which the azulene effect on stilbene isomerization is assumed to have its origin in the interaction of azulene with $^3p^*$ was rejected.[32d,35] However, more recent studies[33c,d,e] showed that $^3t^* \rightleftharpoons {}^3p^*$ equilibration and quenching of $^3t^*$ only is not a unique mechanism for the interpretation of the temperature dependence of the azulene effect on stilbene triplet decay. An alternative mechanism involving the quenching of $^3p^*$ to ^1t was proposed, and the mechanism is strongly supported by the observation that both stilbene isomers are nonvertical acceptors of triplet energy.

The mechanism in Scheme I leads to the following equations. When the steady-state approximation is made on the excited species and the deoxygenated solution is directly irradiated,

$$\Phi_c^0/\Phi_c = 1 + k_{az}[Az]/k_d \tag{3}$$

and in the triplet-sensitized photoisomerization,

$$\Phi_c^0/\Phi_c = (k_1/k_2)(1 + k_{az}[Az]/k_d) \tag{4}$$

and

$$([\mathrm{trans}]/[\mathrm{cis}])_{\mathrm{pss}} = (k_1/k_2)(\alpha/1 - \alpha)\left(1 + \frac{k_{az}[Az]}{\alpha k_d}\right) \tag{5}$$

where subscripts indicate the photostationary-state condition. The biacetyl-sensitized ratio, k_1/k_2, in solution is assumed to be unity, with excitation transfer to either isomer being a diffusion-controlled rate. A linear relationship derived in (4) becomes exactly the same as (3). Equations 2, 3, and 4 clearly indicate that the slope for the direct and sensitized isomerization should be equal to $k_q = k_{az}/k_d$ as observed in our experiments. We therefore conclude that azulene quenches the trans triplet excited state with the diffusion-controlled rate and the lifetime of quenched species can be calculated from the above results ($\tau = 1/k_d$, $k_q = k_{az} \div k_{diff}$). The slope/intercept ratio times α in (5) was exactly the same as the slope ($k_q = k_{az}/k_d$) of the Stern–Volmer plots obtained from (3) and (4) (Figure 1). These azulene quenching results, therefore, indicate that direct photoisomerization of BPyE occurs on the triplet surface.

Nanosecond Laser Spectroscopy. In order to obtain the quantum yields of intersystem crossing and information on trans ⇌ cis isomerization mechanism, laser flash photolysis was carried out. The processes in Scheme II are considered in the laser flash photolysis.

All the triplet states formed decay through intersystem crossing to the ground state, i.e.,

$$\Phi'_{c\to t} + \Phi'_{t\to c} = 1.0$$

and

$$\Phi_c{}^{obsd} = \Phi'_{t\to c} \times \Phi_{isc} \tag{6}$$

where, $\Phi_c{}^{obsd}$ is the observed quantum yield of trans → cis isomerization, $\Phi'_{t\to c}$ is the fraction of triplet states that decay to ^1c (i.e., $\Phi'_{t\to c}$ is the same as $(1 - \alpha)$, 0.43, in the direct and biacetyl-sensitized photoisomerization), and Φ_{isc} is the intersystem crossing quantum yield for the trans isomer.

From Scheme II, the difference absorption coefficient, $\Delta\epsilon_{obsd}(t)$, the difference between absorption after decay and ground-state absorption (initial absorption) on laser flash photolysis, is calculated by

$$\Delta\epsilon_{obsd}(t) = \Phi_{isc}\epsilon_T e^{-t/\tau_T} + \Phi_{isc}\Phi'_{t\to c}\epsilon_{cis}(1 - e^{-t/\tau_T}) + \epsilon_{trans}\Phi_{isc}\Phi'_{c\to t}(1 - e^{-t/\tau_T}) + (1 - \Phi_{isc}) - \epsilon_{trans} \tag{7}$$

$$= \Phi_{isc}(\epsilon_T - \epsilon_{trans})e^{-t/\tau_T} + \Phi'_{t\to c}\Phi_{isc}(\epsilon_{cis} - \epsilon_{trans})(1 - e^{-t/\tau_T}) = \Phi_{isc}(\epsilon_T - \epsilon_{trans})e^{-t/\tau_T} + \Phi_c{}^{obsd}\Delta\epsilon_{c-t}\,(1 - e^{-t/\tau_T}) \tag{8}$$

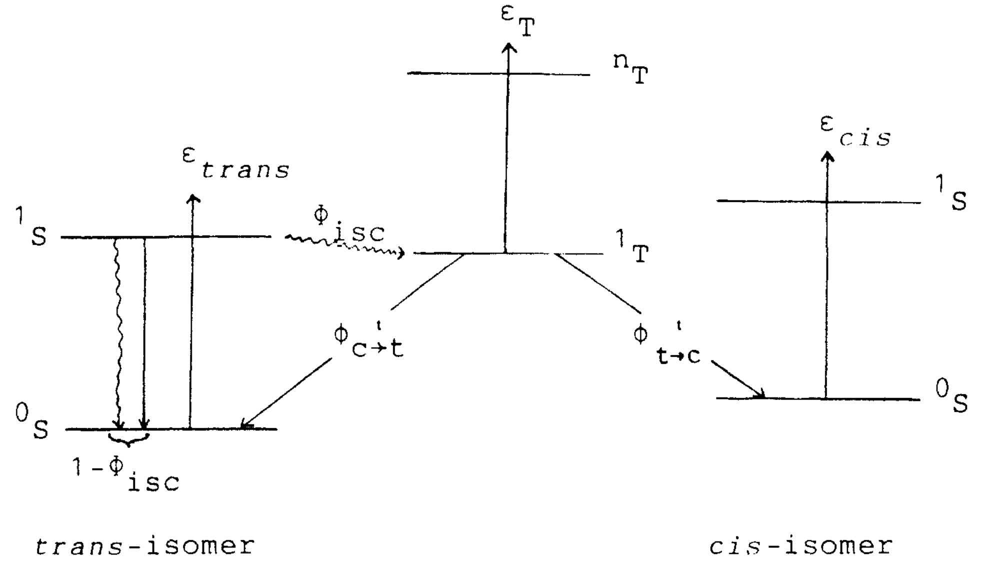
where ϵ_T is the extinction coefficient of triplet–triplet absorption of the trans isomer, ϵ_{trans} and ϵ_{cis} are the extinction coefficient of the ground-state absorption of trans and cis isomers, respectively, t is the scanning time of transient absorption (oscilloscope scanning time), τ_T is the lifetime of the triplet state for trans isomer, and $\Delta\epsilon_{c-t}$ is the difference absorption coefficient between cis and trans ground-state absorption ($\epsilon_{cis} - \epsilon_{trans} \simeq -8000$ M^{-1} cm^{-1}). In (7), the first term is triplet–triplet absorption of trans after intersystem crossing, the second and third terms are the ground-state absorption of cis after isomerization and trans after decay from the triplet state, the fourth term is ground-state absorption of trans after decay from the excited singlet state, and the fifth term is the initial laser flash absorption by the ground-state trans isomer.

---

(34) Gennari, G.; Cauzzo, G.; Galiazzo, G. *J. Phys. Chem.* **1977**, *81*, 1551.

(35) (a) Saltiel, J.; Thomas, B. *J. Am. Chem. Soc.* **1974**, *96*, 5660. (b) Saltiel, J.; Thomas, B. *Chem. Phys. Lett.* **1976**, *37*, 147.

Scheme II. Radiative and Nonradiative Processes in Laser Flash Photolysis



The difference absorbance between absorption after decay and the initial ground-state absorption in Scheme II, $\Delta A_{\mathrm{obsd}}(t)$, can be calculated by (9) with (8) and can be obtained directly by

$$\Delta A_{\mathrm{obsd}}(t) = \Delta\epsilon_{\mathrm{obsd}}(t)C_e l \qquad (9)$$

oscillograms on laser flash photolysis from the reported methods[36] where C_e is the concentration of the excited singlet state and is assumed to be equal to the laser power (absorbed photon no./unit volume, in einsteins, then C_e is 8.33×10^{-6} M) and l is the path length of photon (l = 3.8 cm).

At $t = 0$ (i.e., immediately after flash photolysis), (8) becomes (10). For *trans*-BPyE, $\Delta\epsilon_{\mathrm{obsd}}$ is equal to zero at 344 nm in methanol and at 286 nm in *n*-hexane, meaning that ϵ_T is equal to $\epsilon_{\mathrm{trans}}$ at these wavelengths. It indicates that just after inter-

$$\Delta\epsilon_{\mathrm{obsd}}(t{=}0) = \Delta\epsilon_{\mathrm{isc}}(\epsilon_T - \epsilon_{\mathrm{trans}}) \qquad (10)$$

system crossing, no decay process of the triplet state has started, and only ${}^nT \leftarrow {}^1T$ absorption is observed at this condition.

At $t = \infty$ (i.e., at the point of complete decay after flash photolysis) and at wavelengths where $\epsilon_T = \epsilon_{\mathrm{trans}}$, we can derive (11) from (8). In this condition, $\Delta\epsilon_{\mathrm{obsd}}$ is calculated following

$$\Delta\epsilon_{\mathrm{obsd}}(t{=}\infty) = \Phi_c{}^{\mathrm{obsd}}\Delta\epsilon_{c-t} \qquad (11)$$

(9) to obtained −3386 M^{-1} cm^{-1} at 344 nm in methanol and −1939 M^{-1} cm^{-1} at 286 nm in *n*-hexane for *trans*-BPyE, respectively. The quantum yields of trans → cis isomerization via the triplet surface at these wavelengths can be calculated by (11), and we obtained $\Phi_c{}^{\mathrm{obsd}}$ of 0.423 in methanol at 344 nm and 0.242 in *n*-hexane at 286 nm, respectively. From these $\Phi_c{}^{\mathrm{obsd}}$ values, the quantum yields of intersystem crossing can be calculated by (6). The intersystem crossing yield, Φ_{isc}, obtained by this method was 0.984 in methanol at 344 nm and 0.564 in *n*-hexane at 286 nm, respectively. The quantum yields of cis → trans isomerization and intersystem crossing for *cis*-BPyE were determined by the same method, and we obtained $\Phi_t{}^{\mathrm{obsd}}$ of 0.189 and Φ_{isc} of 0.34 in methanol at 321 nm.

These quantum yields of trans → cis isomerization and intersystem crossing for *trans*-BPyE determined by laser flash experiment at room temperature (24 ± 1 °C, temperature had been controlled) were about the same as those determined by the direct and biacetyl-sensitized photoisomerization (Table I, eq 1). The calculated quantum yields for *cis*-BPyE determined by the laser flash experiment, however, are different from the values obtained by the direct and biacetyl-sensitized photoisomerization because the cis → trans isomerization process competes with the cis → DHP process.

Table VI. Molar Extinction Coefficients of Maximum Triplet–Triplet Absorption Bands of BPyE

substance	wavelength, nm	ϵ_T, M^{-1} cm^{-1}
trans-stilbene[a]	378	3.4×10^4
trans-stilbene-d_{12}[a]	378	2.8×10^4
4,4′-dichlorostilbene[a]	359	2.8×10^5
cis-BPyE[b]	336	9.2×10^3
trans-BPyE[c]	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

[a] From ref 38. [b] Our experimental results in methanol at room temperature. [c] In *n*-hexane at room temperature.

From (8) and (9), the plot of absorbance(t) vs. e^{-t/τ_T} shows linearity. We can calculate the lifetime of the triplet state from the slope of this plot. The triplet decay (${}^nT \rightarrow {}^1T$) curves (at 376 nm for *trans*-BPyE) are exactly matched by the ground-state depletion curves (at 344 nm for trans) measured in methanol by the laser flash experiment, giving the same 160 ns for *trans*-BPyE and 250 ns for *cis*-BPyE decay time at room temperature (Figure 2). The triplet lifetime of *trans*-BPyE thus obtained is exactly the same as the calculated triplet lifetime ($1/k_d$ = 160 ns) by azulene quenching studies (Table V). These observations must be a direct evidence for the trans ⇌ cis isomerization mechanism via the triplet state. In figure 2, we used a differential amplifier in cases of a and b and calibrated the base line for the scattered light. However, we did not use a differential amplifier in cases of c and d in which scattered light is also observed. At 303 nm for *cis*-BPyE (in Figure 2d), we can not directly use $\Phi_t{}^{\mathrm{obsd}}$ by using (10) because $\epsilon_T \neq \epsilon_{\mathrm{cis}}$ (because $\Delta\epsilon_{\mathrm{obsd}}$ (t = 0) ≠ 0). Equation 11 can be used when $t = \infty$ because the signal in d returns to the original value after 0.95 μs. This oscillogram suggests $\Phi_t = 0$ or $\Delta\epsilon_{t-c} = 0$ since $\Delta\epsilon_{\mathrm{obsd}}$ ($t = \infty$) = $\Phi_t\Delta\epsilon_{\mathrm{trans-cis}} = 0$ at 303 nm. At other wavelengths, however, the signal does not return to the original value after the complete decay. It indicates that the value of Φ_t is not zero, but the value of $\Delta\epsilon_{\mathrm{trans-cis}}$ is nearly zero at 303 nm because *cis*- and *trans*-BPyE have isosbestic points in the ground-state absorption at 301 nm.

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. The observed spectra are shown in Figures 3–5 along with the UV spectrum (ground-state absorption). The difference absorption coefficients at each wave-

---

[36] (a) McClure, D. S. *J. Chem. Phys.* **1951**, *19*, 670. (b) Hodgkinson, K. A.; Munro, I. H. *J. Phys. B* **1973**, *6*, 1582. (c) Labhart, H. *Helv. Chim. Acta* **1964**, *47*, 2279. (d) Heinzelmann, W.; Labhart, H. *Chem. Phys. Lett.* **1969**, *4*, 20. (e) Bebelaar, D. *Chem. Phys.* **1974**, *3*, 205.

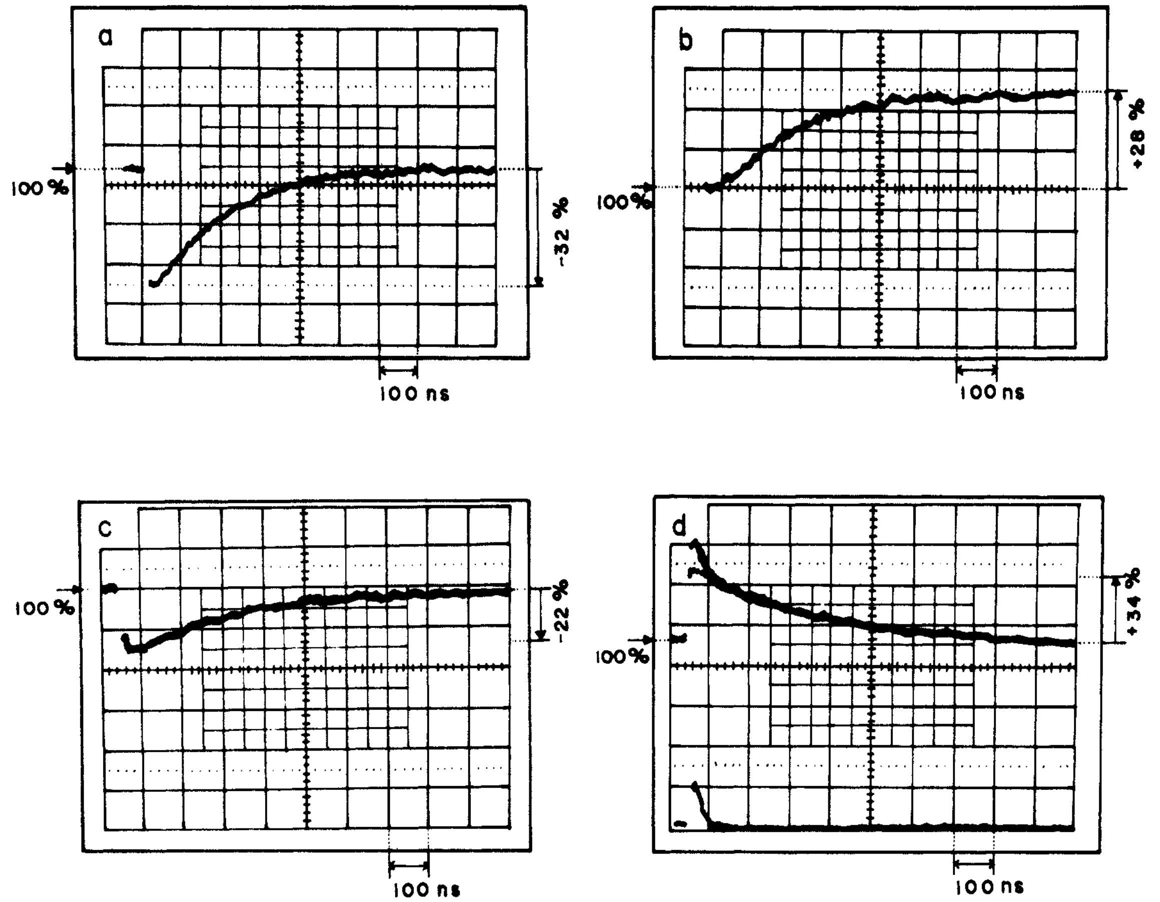


Figure 2. Nanosecond laser spectroscopy of BPyE in methanol at room temperature: a, the triplet decay curve of *trans*-BPyE at 376 nm; b, the *trans*-BPyE depletion curve; c, the triplet decay curve of *cis*-BPyE at 676 nm; d, the *cis*-BPyE depletion curve.

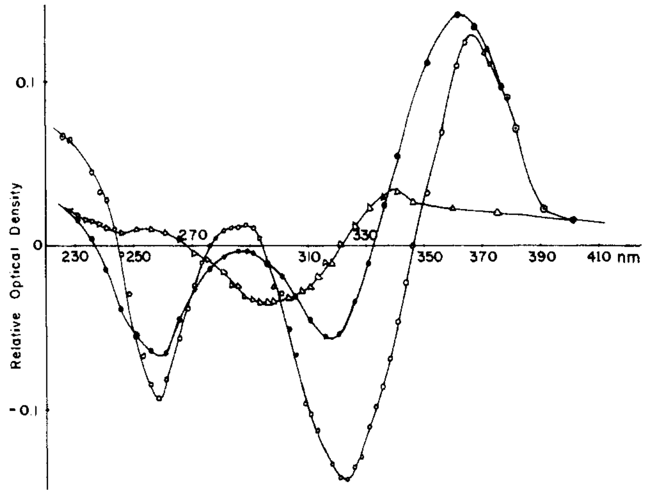


Figure 3. Short-lived transient absorption spectra (difference absorption spectra) at $t = 0$ (i.e., immediately after flash photolysis): *trans*-BPyE in *n*-hexane and in methanol (⊙); *cis*-BPyE in methanol (△).

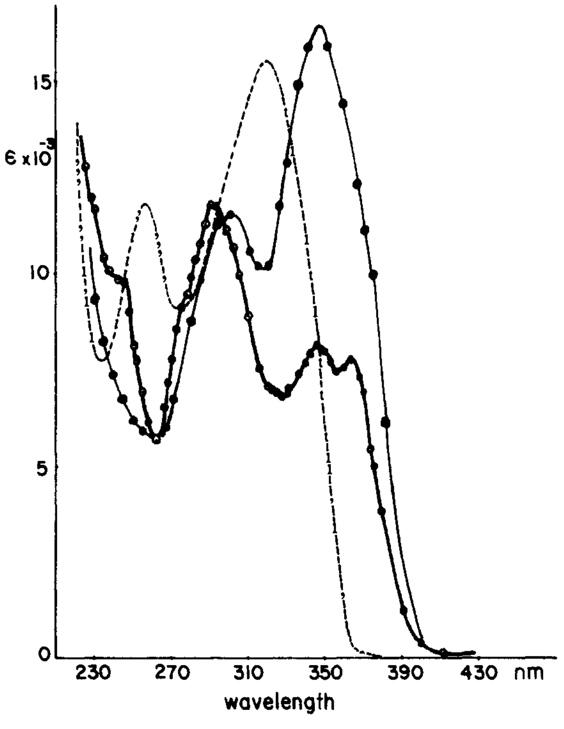


Figure 4. UV absorption (---) and triplet–triplet absorption spectra of *trans*-BPyE in *n*-hexane (●) and in methanol (⊙).

lengths ($\Delta\epsilon_{\mathrm{obsd}}(t = 0)$) are determined at $t = 0$ (i.e., immediately after flash photolysis) by the reported methods.[36] In this case ($t = 0$), the difference absorption coefficient can be obtained after normalization by use of 5600 M^{-1} cm^{-1} for *trans*-BPyE at 376 nm and 3200 M^{-1} cm^{-1} for *cis*-BPyE at 620 nm as a reference, respectively. The determined triplet–triplet absorption coefficients (ϵ_T) at $t = 0$ by (10) are listed in Table VI along with the absorption maxima. The extinction coefficient of the 1,2-benzanthracene triplet–triplet absorption band[37] which has 2.0×10^4 M^{-1} cm^{-1} at 455 nm was also determined for reference purposes.

Herkstroeter and McClure[38] observed the $^{n}\mathrm{T} \leftarrow {}^{1}\mathrm{T}$ absorption of stilbenes in a rigid glass at 77 K by nanosecond flash photolysis

---

(37) McNeil, R.; Richards, J. T.; Thomas, J. K. *J. Phys. Chem.* **1970**, *74*, 2290.

(38) Herkstroeter, W. C.; McClure, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 4522.

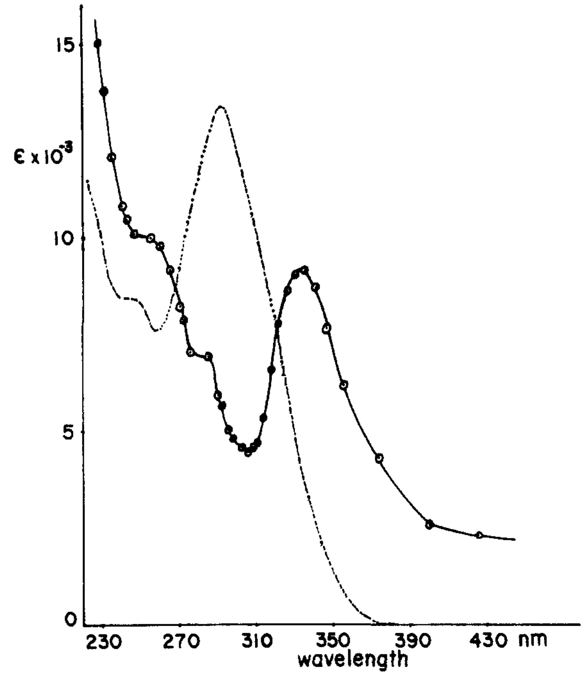


Figure 5. UV absorption (---) and triplet-triplet absorption spectra (⊙) of *cis*-BPyE in methanol.

but they could not observe $^{n}T \leftarrow {}^{1}T$ absorption in fluid solution at room temperature. However, we observed strong $^{n}T \leftarrow {}^{1}T$ absorption for *trans*- and *cis*-BPyE in the fluid solution at room temperature just like in the nitro-substituted stilbenes.[39,40] in which nitro groups enhance the rate of the intersystem crossing. Nitroarmatics very often show only phosphorescence and no fluorescence. In the presence of nitro substituents, the intersystem crossing is enhanced to such a degree that triplet states are populated. Intersystem crossing enhancement is entirely associated with the participation of (n,π*) states of nitro groups in the decay processes. The charge-transfer character 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 much weaker triplet-triplet absorption at low temperatures.[40]

The transient species of stilbene generated by the flash photolysis in glassy matrices at 77 K have previously been identified as triplet states.[38,41] The transient spectra (difference absorption spectra) of *trans*-BPyE in nonpolar and polar solvents show a similar shape and absorption maximum (Figure 3) as shown in the nitro-substituted stilbenes.[39] The solvent shift of the transient absorption (triplet-triplet absorption) in nitro-substituted silbenes is unusually large and is accompanied by a change in the shape of the absorption spectra. In order to explain the solvent shift, Fischer and co-workers[42] assumed that the lowest triplet state for the nitro-substituted stilbenes changes from ^{3}(n,π*) to ^{3}(π,π*) in character as the solvent polarity increases. In BPyE flash photolysis, the triplet-triplet absorption maxima are blue-shifted as the polarity of the medium increases (Figure 4 and Table VI). The triplet-triplet absorption spectra also show fine structure and the shape of the spectra changes (Figure 4) as the medium is changed from *n*-hexane to methanol. These effects may be due to the increase of the energy gap between ^{3}(n,π*) and lowest ^{3}(π,π*) as the polarity of the medium increases in contrast to nitro-substituted stilbenes.

From these results, it is concluded that the transient of BPyE is a triplet state and direct trans ⇌ cis photoisomerization of BPyE proceeds through the triplet excited state in contrast to stilbene.

Conclusions

Photochemical trans ⇌ cis isomerization of BPyE which has both the (n,π*) state and (π,π*) state on direct excitation is strongly affected by the polarity of solvents. Intersystem crossing is enhanced because the ^{1}(π,π*) state and the lowest ^{1}(n,π*) state are extensively mixed as the polarity of solvents increases. Azulene quenching on the photoisomerization and nanosecond laser spectroscopy results also indicate an efficient intersystem crossing on direct excitation of BPyE in contrast to stilbene and their aza analogues. It is therefore concluded that the photoisomerization of BPyE on direct excitation occurs from the triplet excited state in contrast to stilbene.

Acknowledgment. This investigation was supported by the Korea Science and Engineering Foundation. We are grateful to Prof. Jack Saltiel of Florida State University for many helpful discussions.

Registry No. *trans*-BPyE, 62141-47-3.

---

(39) Bent, D. V.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1974**, *78*, 446.

(40) Goerner, H.; Schulte-Frohlinde, D. *Ber. Bunsenges Phys. Chem.* **1978**, *82*, 1102.

(41) Heinrich, G.; Blume, H.; Schulte-Frohlinde, D. *Tetrahedron Lett.* **1967**, *47*, 4693.

(42) Gegiou, D.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907.

(43) Nakashima, N.; Yoshihara, K. *J. Chem. Phys.* **1982**, *77*, 6040.

Stereoselectivity in the Photolysis of Diastereomeric Diazene Surfactants in Aggregated Media[1]

N. A. Porter,* E. M. Arnett,* W. J. Brittain, E. A. Johnson, and P. J. Krebs

*Contribution from the Department of Chemistry, Duke University,
Durham, North Carolina 27706.* *Received August 2, 1985*

Abstract: *meso*- and (±)-bis(cyanododecanoyl)diazene free diacids and their dimethyl esters have been photolyzed in chlorobenzene solution, in water above and below their cmc's, and in bilayer vesicles with dipalmitoylphosphatidylcholines. In water above the cmc and in chlorobenzene there is sharply differentiated stereoselectivity in the product ratios of the free diacid diastereomers, the (±) always giving the greater retention. The (±) diastereomer also shows the greater driving force toward aggregation in micelles and in monolayers where its surface properties are dramatically different from those of the meso isomer. A simple explanation is proposed to relate the aggregation properties to the stereochemistry. The possible broad significance of these results to biochemistry is suggested.

Many important biological processes are stereoselective and take place at the interfaces of aggregated assemblies such as membranes, lipid bilayers, or organelles rather than in isotropic media. Considering that form and function are usually correlated

0002-7863/86/1508-1014$01.50/0