

The *trans* → *cis* Photoisomerization and Fluorescence of *trans* 1,2-Bispyrazylethylene: pH, Salt and Heavy Atom Effects

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The *trans*→*cis* photoisomerization and fluorescence of *trans*-1,2-bispyrazylethylene were investigated in various conditions. The quantum yields of the *trans*→*cis* photoisomerization and the fluorescence intensity of *trans*-1,2-bispyrazylethylene decrease on going from neutral to acidic or basic solutions. The quantum yields of photoisomerization, however, are little affected by changing the concentration of salt while the fluorescence intensity increases as the concentration of salt increases. pH and salt effects on the energy levels of ${}^1(n, \pi^*)$ and ${}^1(\pi, \pi^*)$ states lead to opposing changes in photoisomerization and fluorescence quantum yields. The heavy atom effect on the fluorescence of 1,2-bispyrazylethylene was also investigated.

Introduction

The photochemical reactions and spectroscopy of nitrogen heterocyclic compounds have received much attention.^{1,2} The introduction of nitrogen atoms into the phenyl rings noticeably affects the photophysical and photochemical behavior of stilbene^{3,4} probably due to the involvement of (n, π^*) states in the reaction mechanism. Because of the proximity of ${}^1(\pi, \pi^*)$ state to the lowest ${}^1(n, \pi^*)$ state, intersystem crossing is tremendously enhanced in pyrazine ($\Phi_{isc} \cong 1.0$) compared to benzene ($\Phi_{isc} \cong 0.25$) and pyridine ($\Phi_{isc} \cong 1.0$).^{5,6}

The 1,2-bispyrazylethylene (BPyE), a tetraazastilbene analogue, is an attractive candidate for spectroscopic and photochemical studies since the compound has both (n, π^*) and (π, π^*) states in contrast to stilbenes. The effect of salt and protonation on the fluorescence of BPyE is investigated in detail to obtain more information on the excited state responsible for the photoisomerization. The possible relationship between the photoisomerization of BPyE and the acid-base equilibria in the excited state is also studied on the basis of recently proposed photoisomerization mechanism of BPyE.⁷

Experimental

Extra pure solvents were used as received or after distillation. *trans*-1,2-Bispyrazylethylene, prepared by the reported method⁸ starting from pyrazine carboxylic acid, was recrystallized from acetone.

Emission spectra were recorded on an Aminco Bowman Spectrophotofluorometer with Aminco XY-recorder. High performance liquid chromatogram was obtained on a Waters Associates Model 244 equipped with Model 6000A solvent delivery system and Model 440 Absorbance detector (254 nm and 280 nm).

The quantum yield measurement techniques have been described in our previous paper.^{7a} Sample solutions (3 ml) for quantum yield determination were pipetted into the ampoules, degassed through three to five freeze-pump-thaw cycles with cooling in liquid nitrogen and sealed. The solutions in the sealed ampoules were irradiated with Hanovia 450 W medium pressure mercury arc lamp (Type 697A36) in a merry-go-round apparatus. Mercury emission line of 366.0 nm was isolated by using Corning glass filters #0-52 and #7-37. Ferrioxalate actinometry was used to monitor the intensity of the exciting light. Quantitative analyses were car-

ried out by reverse phase HPLC techniques: μ -Bonadapak C₁₈ (3.9 mm I.D. × 30 cm) column; water/methanol/tetrahydrofuran (v/v, 40/40/3) eluent. Quantum yields of isomerization were determined using low conversion (less than 5%) to prevent appreciable back-reaction.

Results and Discussion

The previous papers indicate that the *trans*-1,2-dipyridylethylenes (DPE's) have two basic centers which display pK_a 's for the first protonation in the range 4.8~5.6 and pK_a 's for the second protonation in the range 2.3~3.6.^{9,10} Since the photoisomerization process of azastilbenes can be quenched or enhanced by changing the pH from >3 to <7, the free base and the conjugate acid have greatly different quantum yields of photoreaction.

The pH and salt effects on the direct photoisomerization of *trans*-BPyE are summarized in Table 1. The pH and salt effects on the fluorescence intensity of *trans*-BPyE are shown in Table 2 and Figure 1. The quantum yields of *trans*→*cis* photoisomerization decrease in the pH lower than 2. The fluorescence intensity of *trans*-BPyE also decreases in the pH lower than 2 and greater than 8. However, the quantum yields of isomerization are little affected by changing the concentration of salt while the fluorescence intensity increases as the concentration of salt increases.

If proton forms a complex with nitrogen atoms of BPyE, the proton will raise the energy of the lowest ${}^1(n, \pi^*)$ state. Because the proton is not expected to affect the energy of ${}^1(\pi, \pi^*)$ state, the intensity of fluorescence originating from the ${}^1(\pi, \pi^*)$ state decreases as the pH reaches near pK_a value. These results are different from those of 3-styrylpyridine¹⁰ and 5-styryl-1,3-dimethyluracil¹¹ which have big energy gap between ${}^1(n, \pi^*)$ state and the lowest ${}^1(\pi, \pi^*)$ state.

Application of the Förster cycle procedure to azastilbenes leads to pK_a^* values in the 1S state being 6~8 pK units higher than those of the ground state. Calculated ionization constants for the three isomeric styrylpyridinium cations in the first excited singlet state are reported in Table 3 together with the experimental results for 1,2-bispyrazylethylene. Fluorimetric titration has confirmed this strong basicity ($pK_a^* \cong 12\sim 13$) when the 1S lifetime is long enough to permit the excited molecule to equilibrate, at least partially, with proton.¹⁰ In BPyE, one has to use pH 13~14 in order to obtain the reaction of the neutral molecule. A two step trend in the plot of

ϕ_{fl} and ϕ_{isc} against pH was observed, the two inflection points corresponding to pK_a and pK_a^* . The fluorescence intensity of *trans*-BPyE also decreases as pH approaches to 8~9. This indicates that BPyE has a pK_a^* value in the range of pH 8~9 in 1S state, 6~8 pK units higher than that of the ground state which is similar to that of 3-styrylpyridine.¹⁰

The fluorescence yield of retinal is enhanced by halide salts such as potassium iodide due to retinal-alkaline metal cation complex formation.¹² The $^1(n,\pi^*)$ -alkaline metal cation complex is not uncommon as shown in the interaction between Li^+ and carbonyl groups.¹³ The addition of alkaline salt, therefore, will diminish the fluorescence intensity of *trans*-BPyE which has the lowest $^1(n,\pi^*)$ state if $^1(n,\pi^*)$ state is fluorescent. However, sodium acetate enhances the fluorescence intensity of *trans*-BPyE indicating that the lowest and fluorescent excited state is $^1(\pi,\pi^*)$ state. If the effect for the lowest $^1(n,\pi^*)$ state at neutral condition by the salts is greater than that of acids, inversion of the energy level between $^1(\pi,\pi^*)$ and $^1(n,\pi^*)$ states is expected and the mechanism of the salts and proton effect on the fluorescence is different (Scheme 1).

Table 1. pH and Salt Effects on the Direct *trans*→*cis* Photoisomerization of BPyE at 366 nm

pH	ϕ_c^*	Concentration of LiCl, M	ϕ_c^*
7.0	0.38	0	0.38
5.0	0.37	5.0×10^{-3}	0.37
3.0	0.14	5.0×10^{-2}	0.35

*Concentration of *trans*-BPyE is 5.0×10^{-3} M and quantum yields are determined in acetonitrile-water (v/v, 7:3).

Table 2. pH and Salt Effects on the Fluorescence of *trans*-BPyE at 366 nm Excitation

pH	I_{fl}/I_{fl}^0 ^a	Concentration of NaOAc, M	I_{fl}/I_{fl}^0 ^b
12.5	0.63	0	1.00
9.0	0.63	2.5×10^{-2}	1.60
8.0	1.00	5.0×10^{-2}	1.80
7.0	1.00	7.5×10^{-2}	1.90
3.0	1.00	1.0×10^{-1}	1.90
1.9	0.85		
1.3	0.45		

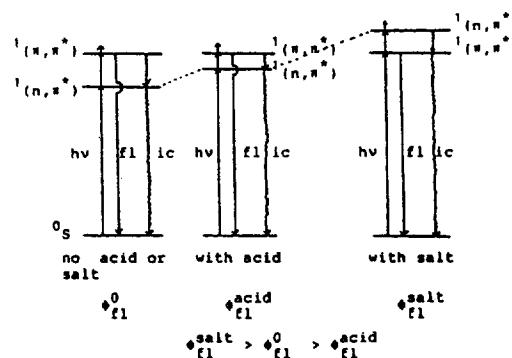
^a I_{fl}^0 is the fluorescence intensity in acetonitrile-water (v/v, 7:3) at pH 7.0. ^bFluorescence spectra are obtained in ethanol at 77K.

Table 3. Basicity of *trans*-Styrylpyridines and *trans*-1,2-Bispyrazylethylene in the Ground and Excited States

Compound	pK_a	pK_a^*
2-StP ^a	4.98 ^a	11.4
3-StP ^a	4.76	12.4
4-StP ^a	5.73 ^a	13.3
BPyE ^c	less than 2	8.9

^aFrom ref. 9a in water-ethanol (v/v, 90:10). ^bFrom ref. 3a in water-ethanol (v/v, 90:10). ^cOur experimental results in water-acetonitrile (v/v, 30:70).

As has already been pointed out, ethyl bromide (heavy atom) causes a 2~3 fold decrease in the lifetime of $^3p^*$ (twisted triplet state) of stilbene.¹⁴ No other enhancement of singlet-triplet intersystem crossing by heavy atoms present in the solvents can be discerned. The lack of a heavy atom effect in the direct photoisomerization of stilbene in ethyl bromide may be due to the short lifetime of $^1t^*$ (transoid singlet state). This phenomenon may also be due to the negligible intersystem crossing of stilbene which has no $^1(n,\pi^*)$ state. The heavy atom effect on the fluorescence of *trans*-BPyE is shown in Figure 2. The fluorescence intensity is lower as the concentration of methyl iodide or potassium iodide increases. The decrease in the fluorescence intensity can be attributed to a shortening of the lifetime of $^1t^*$ of BPyE when the heavy atom is added. This could also be due to an increase in the rate of intersystem crossing. However, fluorescence intensity is in-



Scheme 1. The salt and proton effect on the energy level between $^1(\pi,\pi^*)$ and $^1(n,\pi^*)$ states and fluorescence quantum yield of *trans*-BPyE.

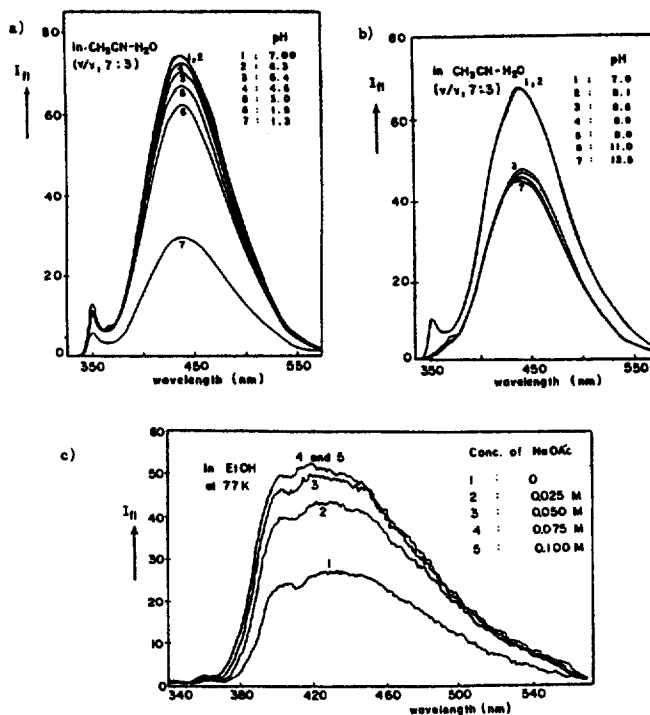


Figure 1. pH and salt effects on the fluorescence of *trans*-BPyE; a, by HCl in water-acetonitrile (v/v, 30:70) at room temperature; b, by KOH in water-acetonitrile (v/v, 30:70) at room temperature; c, by NaOAc in ethanol at 77K.

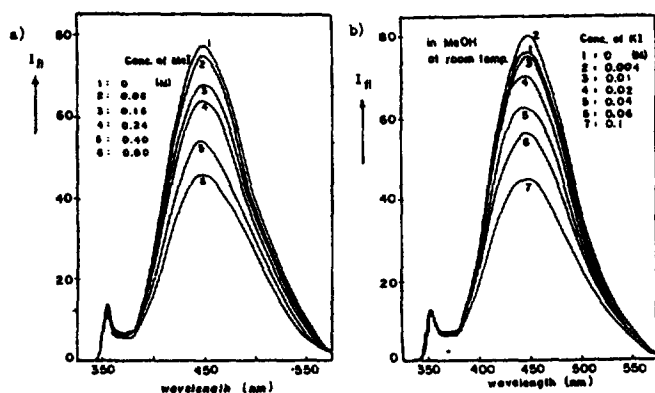


Figure 2. Heavy atom effect on the fluorescence of *trans*-BPyE in methanol at room temperature; a, by MeI; b, by KI.

creased when the concentration of potassium iodide is very small. This phenomenon is due to the salt effect on the fluorescence by alkaline salt. As the concentration of potassium iodide increases, the fluorescence intensity decreases because of the heavy atom effect. When methyl iodide is added, the intensity of fluorescence decreases showing normal heavy atom effect.

The fluorescence efficiency of *trans*-BPyE at 77K ($\phi_f \cong 0.025$) differs from those of *trans*-styrylpyridines and *trans*-1,2-dipyridylethylenes ($\phi_f \cong 1.0$ at 77 K). The triplet formation in BPyE is also observed by laser flash photolysis at room temperature^{7a} in contrast to styrylpyridines and 1,2-dipyridylethylenes. Azulene quenching studies indicate that the triplet state is the reactive state in photoisomerization.^{7a} From these results, therefore, it is concluded that the intersystem crossing of BPyE is an important process at room temperature and the direct photoisomerization of BPyE proceeds through the triplet manifold in contrast to stilbenes, azastilbenes, and diazastilbenes.

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Surface-enhanced Raman Scattering on Chemically Prepared Silver Film for Trace Analysis

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Analytical capability of surface-enhanced Raman scattering has been evaluated. Silver films prepared by homogeneous chemical reduction were used as the substrate. Detection limits for *p*-nitrobenzoic acid, thiophenol and rhodamine 6G were around 10~100 pg.

Introduction

Raman spectroscopy is a useful technique for the analysis

of organic materials.^{1,2} Like the infrared spectroscopy, various structural information, particularly the presence of certain functional groups, is available from the Raman spectra. Ap-