1, 2-비스피라질 에틸렌의 합성과 분광학적 성질에 대한 연구

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Synthesis and Spectral Properties of 1, 2-Bispyrazyl Ethylene

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요 약. 메틸 피라진과 피라진산으로 부터 새로운 화합물 1,2-비스피라질 에틸렌을 합성하여 기기분석과 원소분석으로 이 화합물의 구조를 확인하였다.

UV-VIS 스펙트럼에서는 예상했던 $(n, \pi^*)^1$ 흡수띠가 흡광도가 강한 $(\pi, \pi^*)^1$ 흡수띠에 묻혀 볼 수가 없었으나 형광에 미치는 염의 효과로 부터 $(n, \pi^*)^1$ 상태가 $(\pi, \pi^*)^1$ 상태와 거의 같은 에너지를 갖고 있음을 알았다. 77°K에서 형광의 양자 수득률은 0.025로서 같은 조건에서 형광 양자 수득률이 1인 스틸벤과 좋은 대조를 이루며 이는 (n, π^*)와 (π, π^*)의 혼합으로 단일 상태에서 삼중 상태로의 intersystem crossing이 효율적으로 잘 일어난다는 것을 말해 준다.

ABSTRACT. A new compound, 1,2-bispyrazyl ethylene, is synthesized starting from pyrazine carboxylic acid and methyl pyrazine. The compound is characterized utilizing UV-VIS, IR, NMR and mass spectra along with elemental analysis.

Spectroscopic properties are studid from UV-VIS and fluorescence spectra. From unusual salt effects on fluorescence spectra, it is believed that $(n, \pi^*)^1$ state has about the same energy as $(\pi, \pi^*)^1$ state. The compound fluoresces from $(\pi, \pi^*)^1$ state with the quantum yield of 0.025 at 77°K compared to near unity for stilbene at the same temperature indicating the efficient intersystem crossing to triplet state, because of strong (n, π^*) and (π, π^*) mixing in the lowest excited state.

INTRODUCTION

The diazines, pyrazine, pyrimidine, and pyridazine, possess two lone pairs of electrons which experience different environments in the different molecules. These compounds all exhibit three $\pi \rightarrow \pi^*$ transitions between 165 and 265 nm along with a low-energy $n \rightarrow \pi^*$ transition[1]. The

theoretical analysis of the nature of lone pairs and the effect of heteroatoms on the electronic spectra of these cmopounds have been some interest to spectroscopists and theoretical chemists[1,2]. A quantum mechanical studies on pyrazine and other diazines show that orbitals of the lone-pair type are in general delocalized throughout the system. These two orbitals interact more or less strongly, depending on geometry

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to raise the energy of the highest-filled "n" orbital and this in turn causes the red shifts in $n \rightarrow \pi^*$ transitions and lead to increase in the Van Vleck paramagnetic contributions[2,3]. This is what is observed experimentally as shown in *Table* 1. Pyrazine shows a distinct and exceptionally strong $n \rightarrow \pi^*$ transition band at 328 nm (ϵ 1, 040) and $\pi \rightarrow \pi^*$ band at 260 nm (ϵ 5, 600).

One of the most important task in photochemical studies is to elucidate the character of the reactive excited states. The excited singlet states often lead to different reaction paths and the character of (n, π^*) and (π, π^*) states are quite different leading to different photoreactions.[4] For example, (π, π^*) state of stilbazole, a stilbene analogue with a nitrogen atom replacing carbon in a benzene ring, undergo *cis-trans* photoisomerization just like stilbene $(\pi, \pi^*)^3$ state but $(n, \pi^*)^1$ state leads to photoreduction of central ethylenic double bond in cyclohexane[5,6]. This photoreduction is not observed in stilbene photochemistry. However, $(n, \pi^*)^1$ state is buried under the strong $(\pi, \pi^*)^1$ band in stilbazole spectra and the evidence of $(n, \pi^*)^1$ reactive state in photoreduction is indirect. Thus 1, 2-bispyrazyl ethylene, a stilbene analogue with pyrazine rings replacing the benzene rings in stilbene, is an attractive candidate for spectroscopic and photochemical studies since the compound is expected to show the well-defined stilbene energy levels plus a distinct (n, π^*) state. The $n \rightarrow \pi^*$ band is expected to be distinct from $\pi \rightarrow \pi^*$ band since $n \rightarrow \pi^*$ band of pyrazine is strong and is located at relatively long wavelength. The λ_{max} of $\pi \rightarrow \pi^*$ band of stilbene which is expected to be about same as that of 1, 2-bispyrazyl ethylene is located at 294 nm (ϵ 27, 950). The compound is synthesized and its spectral properties are studied.

EXPERIMENTAL

Synthesis of *trans*-1, 2-Bispyrazyl Ethylene

Methyl pyrazinoate was synthesized from pyrazine carboxylic acid (Aldrich Chemicals) with 77 % yield by the method reported[7]. Controlled reduction of methyl pyrazinoate with lithium aluminum hydride in tetrahydrofuran[8] yielded pyrazine aldehyde with 35 % yield.

Pyrazine aldehyde (3. 2 g), methyl pyrazine (12 ml) (Aldrich Chemicals), and acetic anhydride (4. 5 ml) (Wako Chemicals) in round bottom flask were refluxed at 150~160°C under the nitrogen atmosphere for 48 hours to get black tar-like products. The solid products obtained on cooling the reaction mixture to room temperature were subjected to vacuum distillation to remove low boiling materials. The coal-like powder remained were sublimed at 160~170 °C under the vacuum (10^{-2} mmHg) to get 1. 9g of yellow product. Decoloration by norite in acetone solution and recrystallization yielded colorless needle-like crystals. m. p 191~2 °C, yield 50 %. Elemental analysis C 65. 5 %, H 4. 59 %, N 30. 0 % (Calc. C 65. 21 %, H 4. 38 %, N 30. 42 %).

Synthesis of *cis*-1, 2-Bispyrazyl Ethylene

0. 184 g(0. 001 mole) of *t*-BPE were dissolved in 90 ml of purified benzene and 0. 182 g (0. 001 mole) of benzophenone was added to the solution as a photosensitizer. Benzene was added to the solution to make the final volume 100 ml. The solution was irradiated in a Rayonet reactor with 350 nm lamp in a Pyrex vessel for 2 hours. Solvent was evaporated and benzophenone was sublimed under the vacuum. *cis*-BPE were extracted with carbon tetrachloride and recry-

Table 1. The singlet-singlet electronic transitions in diazines.

	$n \rightarrow \pi^*$(nm)	ϵ	$\pi \rightarrow \pi^*$	ϵ
Pyridine	270	450	251	2, 000
Pyrazine	328	1, 040	260	5, 600
Pyrimidine	298	325	243	2, 030
Pyridazine	340	315	251	1, 400

stallized from the same solvent. m. p 100. 5～ 101. 5 °C, yield 85%.

Materials

Ethanol. 5 g of magnesium turnings were added to 60 ml of absolute ethanol (Wako Chemicals) and refluxed after adding a few drops of carbon tetrachloride. After 2 hours, added 900 ml of absolute ethanol and refluxed for 8 hours and distilled collecting middle portion (b. p 77. 5 °C). Ethanol so prepared was transparent to UV above 210 nm.

Benzene. Analytical grade benzene (Merck) was stirred with concentrated sulfuric acid for several hours. The colored sulfuric acid was separated and the process was repeated until no coloration of sulfuric acid layer was observed. The benzene was washed with water and potassium carbonate solution in that order twice, then dried with magnesium sulfate and distilled over phosphorous pentoxide collecting middle portion (b. p 80 °C). The benzene was redistilled if the phosphorous pentoxide was colored during the distillation.

Benzophenone. Benzophenone (Merck) was recrystallized three times from ethanol. m. p 45. 9～46. 0 °C.

Methods

Nuclear magnetic resonance spectra were measured on a Varian T-60A spectrometer against tetramethylsilane standard in deuterochloroform or in carbon tetrachloride. Infrared spectra were measured on a Perkin-Elmer Model 267 spectrophotometer in carbon tetrachloride or chloroform solvents. Potassium bromide pellets were also used.

Ultraviolet-Visible spectra were recorded on a Cary 17 spectrophotometer.

Mass spectra were recorded on a Finnigan 1015 mass spectrometer and elemental analyses were carried out at KIST.

Fluorescence spectra were measured on a

Perkin-Elmer spectrofluorometer. The quantum yield of fluorescence (Φ_F^s) of dilute BPE solutions were calculated by the following equation as described previously[10]. Φ_F^r is the fluorescence quantum

$$\Phi_F^s = \Phi_F^r \cdot \frac{I_F^s(\bar{\nu})d\bar{\nu}}{I_F^r(\bar{\nu})d\bar{\nu}} \cdot \frac{OD_\lambda^r}{OD_\lambda^s} \cdot \frac{n_r^2}{n_s^2}$$

yield of a reference compound, riboflavin tetrabutyrate. I_F and n are fluorescence intensity (in arbitrary unit) and refractive index of solvent respectively. Optical densities (OD) of reference and sample compounds were kept identical to minimize errors due to Maclaurin's approximation and bandpass differences between the absorption and fluorescence measurements.

RESULTS AND DISCUSSIONS

Characterization of *trans* and *cis*-BPE.

Elemental analyses of both *trans* and *cis*-BPE synthesized agree with the molecular formula of BPE, $C_{10}H_8N_4$.

Mass spectra show the parent peak of m/e 184 which is the molecular weight of BPE. The fragmentation pattern (*Table* 2) indicates the presence of pyrazine moiety in the molecule. The spectra for both *trans*- and *cis*-BPE are exactly same as expected.

The infrared spectrum of *trans*-BPE shows a 975 cm^{-1} band characteristic of the out-of-plane C-H bending vibrations of *trans*-olefins. Bands at 854, 1,325, 1,517, and 1,575 cm^{-1} indicate the presence of pyrazine rings. The spectrum

Table 2. Mass spectral fragmentation data for bispyrazyl ethylene.

m/e	% of base peak	
184	64. 2	Molecular peak
157		M-HCN
130	100	M-2HCN
105	9. 3	M-Pyrazine ring
79	8. 3	Pyrazine ring

of cis-BPE shows a 725 cm^{-1} band characteristic of cis-olefins along with 845, 1,333, 1,475, 1,510, and 1,560cm^{-1} of pyrazine rings. A band at 1,640 cm^{-1} is assigned to C=C of central double bond which is not infrared active

in trans-BPE and was not observed in the spectrum of trans-BPE.

The nmr spectra of trans-and cis-BPE are shown in Figs. 1 and 2, and summarized in Table 3. The spectra agree with the structure
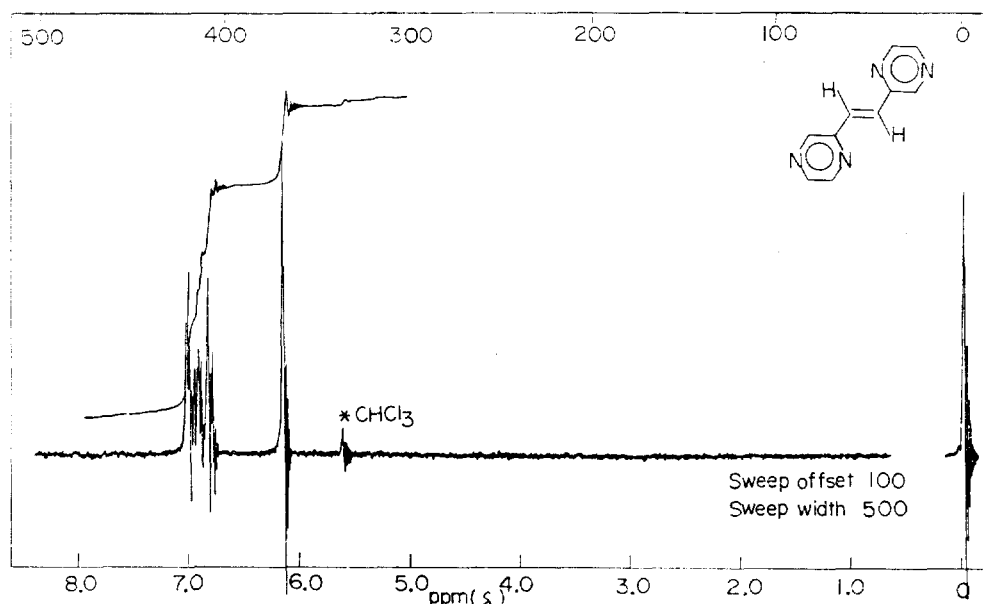

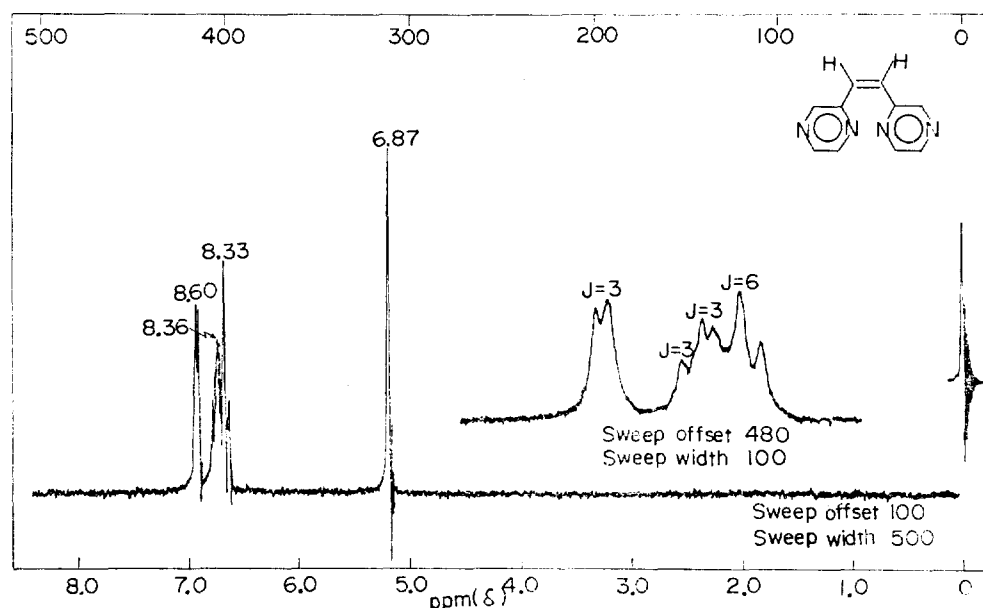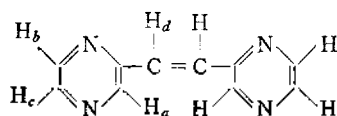Fig. 1. NMR spectra of trans-bispyrazyl ethylene (Sweep offset 100Hz).

Fig. 2. NMR spectra of cis-bispyrazyl ethylene (Sweep offset 100 Hz).

Table 3. NMR spectral data for bispyrazyl ethylene.

| | Chemical shift (ppm) | | | | Coupling constant(H$_z$) | | |
	H_a	H_b	H_c	H_d	J_{ab}	J_{bc}	J_{ac}
trans-BPE	8.66	3.56	8.46	7.83	~1.5	~2.5	0
cis-BPE	8.63	8.46	8.37	6.93	~1.5	~2.5	0

Solvent: CDCl$_3$, Reference: TMS

of BPE.

Thus the synthesized compounds are *trans*-and *cis*-bispyrazyl ethylene.

Absorption Spectra. The absorption spectra of *trans*-and *cis*-BPE, shown in *Fig.* 3, are similar to those of their stilbene counterparts with less vibrational structure because of better solute-solvent interaction and (n, π^*)-(π, π^*) mixing in heteroaromatic ststems.

The first maxima, occurring at 324 nm (ϵ 22,500) for *trans* isomer and at 295nm (ϵ 13,000) for *cis* isomer, are assigned as $\pi \rightarrow \pi^*$ K band because of their large molar absorptivities and a slight spectral change with solvent variations.

The first maximum for *trans*-BPE lies at a little longer wavelength than that of *trans* stilbene[11]. This indicates that the excitation in the lowest planar excited states of BPE is delocalized over the entire chromophore, two pyrazine rings and central ethylenic bond. The longer λ_{max} in BPE compared to that of stilbene indicates also the extensive overlap of the π-orbitals as well as the significant contribution of nitrogen lone-pair elecrons to π-conjugation. Thus the delocalization of the lone-pair type orbitals throughout the σ system in pyrazine rings not only causes the red shifts in $n \rightarrow \pi^*$ transitions in diazines but also causes the batho-
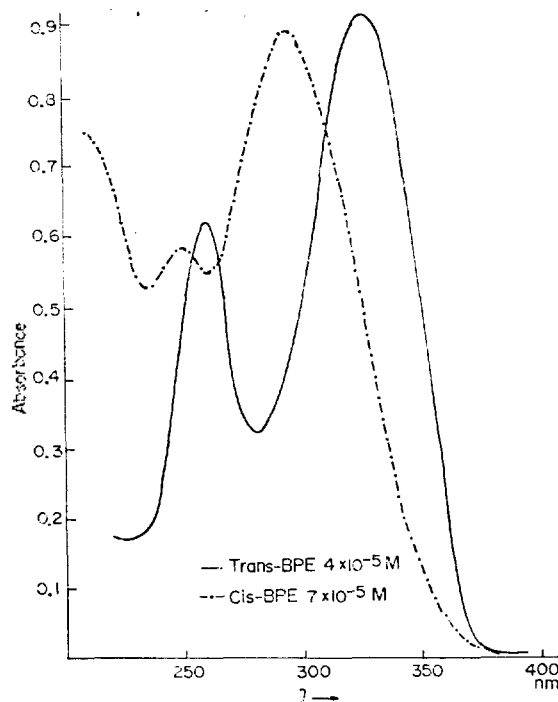

Fig. 3. Spectra of bispyrazyl ethylene in ethanol.

chrom ic shiftin $\pi \rightarrow \pi^*$ transitions in BPE.

The B bands of BPE corresponding to the B band of pyrazine ring give second maxima at 258 nm (ϵ 15,500) for *trans* isomer and at 250 nm (ϵ 8,400) for *cis*-BPE.

The $n \rightarrow \pi^*$ transitions of BPE are expected to red shift substantially from those of pyrazine because of extensive π-conjugation lowering the energy level of lowest unoccupied π^* orbital.

and the intensity of $n \rightarrow \pi^*$ band of BPE is expected to be twice that of pyrazine because of two pyrazine rings in a molecule of BPE. However, ethanol solution of BPE show no distinct $n \rightarrow \pi^*$ band in ultraviolet spectra. Conceivably BPE may have the lowest (n, π^*) excited state which should be strongly localized near nitrogen and is not influenced by the extended π-conjugation because the excitation energy is not delocalized over the entire molecule but localized in a pyrazine ring. Thus $n \rightarrow \pi^*$ transitions of BPE may occur at approximately same wavelength, 328 nm, as those of pyrazine itself and consequently the $n \rightarrow \pi^*$ bands are buried under the strong $\pi \rightarrow \pi^*$ transition bands. Thus $(n, \pi^*)^1$ and $(\pi, \pi^*)^1$ states are very close and efficient mixing of these two states is expected and consequently a distinct (n, π^*) band is missing.

Fluorescence Studies. The lowest excited singlet and triplet states are the starting points of most organic photochemical processes in condensed phase[4]. The study of the nature of these states, therefore, is one of the most important tasks in photochemistry. One of the best and simplest methods for the study is emission spectroscopy.

When BPE is excited by light absorption, the following kinetic scheme should adequately describe the deactivation of the lowest singlet and triplet states where k_i, k_d, k_f, k_{ST}, k_{is} (k_{is}'), k_p, and k_{ST}' are the specific rate constnnts for internal conversion to S_1, internal conversion to S_0, fluorescence, intersystem crossing to T_1, isomerization, phosphorescence, and intersystem crossing to S_0. S and T represent singlet and triplet state respectively.
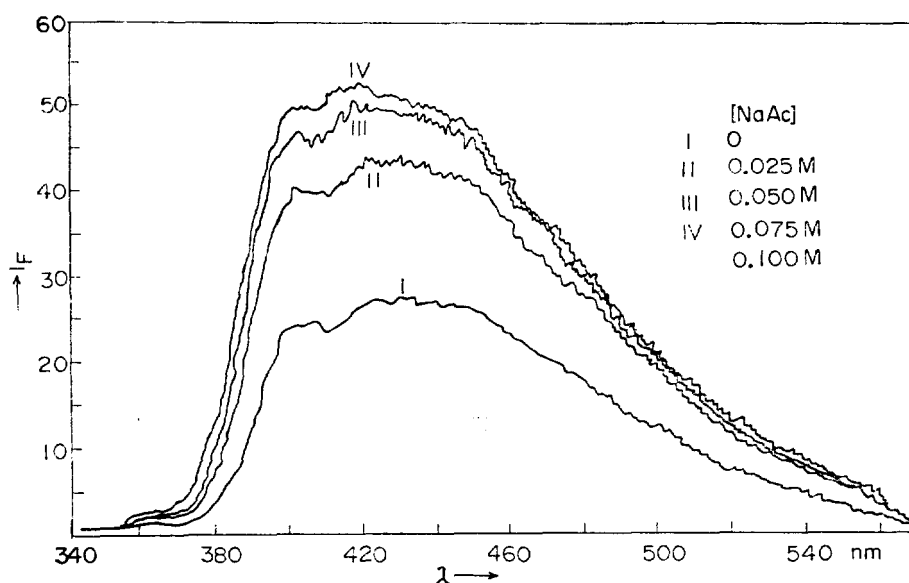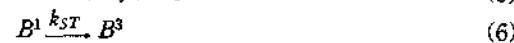
$$B_0 + h\nu \xrightarrow{I_a} B^1 \ (n, \pi^*) \text{ or } B^1 \ (\pi, \pi^*) \quad (1)$$

$$B^1(n, \pi) \xrightarrow{k_i} B^1 \ (\pi, \pi^*), \ E \ (n, \pi^*)^1 > \\ E(\pi, \pi^*)^1 \quad (2)$$

$$B^1 \ (\pi, \pi^*) \xrightarrow{k_i} B^1 \ (n, \pi^*), \ E(\pi, \pi^*)^1 > \\ E(n, \pi^*)^1 \quad (3)$$

$$B^1 \xrightarrow{k_d} B_0 \quad (4)$$

$$B^1 \xrightarrow{k_F} B_0 + h\nu_F \quad (5)$$

$$B^1 \xrightarrow{k_{ST}} B^3 \quad (6)$$

$$B^1 \xrightarrow{k_{is}} \text{Isomer} \quad (7)$$

$$B^3 \xrightarrow{k_p} B + h\nu_p \quad (8)$$

$$B^3 \xrightarrow{k_{is}'} \text{Isomer} \quad (9)$$

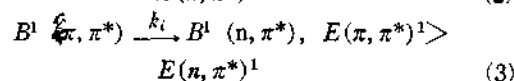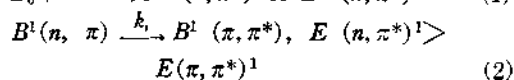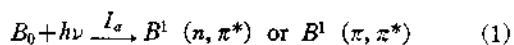$$B^3 \xrightarrow{k_{ST}'} B_0 \quad (10)$$

Fig. 4. Salt effect on the fluorescence of *trans*-bispyrazyl ethylene.

The fluorescence spectrum of *trans*-BPE in ethanol matrix at 77°K is broad with λ_{max} at around 430nm as shown in *Fig.* 4. The quantum yield is 0.025 for 366 nm excitation and 0.015 for 313 nm excitation. These values are very low compared to unity for *trans* stilbene at the same conditions[12]. The drastic decrease of fluorescence efficiency in BPE compared to *trans* stilbene demands some processes to deactivate the excited BPE with a rate much faster than fluorescence. An approximate calculation[4] of the lifetime for *trans*-BPE fluorescence is ca. 7.×10⁻⁹ sec; consequently, the lifetime for what amount to a net process of radiationless decay is about 1.8×10⁻¹⁰ sec or less. The quantum yield of fluorescence is expressed from above equations as:

$$\Phi_F = \frac{k_F}{k_d + k_F + k_{ST} + k_{is}}$$

In ethanol glass at 77°K, k_{is} is negligibly small. Therefore, it is very likely that the efficient intersystem crossing from S_1 to T_1 is responsible for low quantum yields of fluorescence. This is very likely because of efficient (n, π^*) and (π, π^*) mixing[13,14] shown by broadening of absorption and emission spectra.

In general, $(n, \pi^*)^1$ states are not fluorescent but the vapor phase $(n, \pi^*)^1 \rightarrow S_0$ fluorescence of benzoquinone and anthraquinone have been observed as well as $(n, \pi^*)^1 \rightarrow S_0$ fluorescence of pyridazine, pyrimidine, and 3,4-benzoquinoline in solution. Thus, it is not clear which of the $(n, \pi^*)^1$ and $(\pi, \pi^*)^1$ states is fluorescent in *trans*-BPE.

The fluorescence is in general quenched by heavy atoms largely due to enhanced $S_1 \rightarrow T_1$ intersystem crossing, and it is particularly effective for aromatic compounds in which only (π, π^*) excited states are involved[15]. However, the fluorescence of retinal is enhanced by halide salts such as potassium iodide due to retinal–M⁺ complex formation where M⁺ is alkaline metal cations[10]. The $(n, \pi^*)^1$–M⁺ complex is not uncommon and the mechanism of interaction between Li⁺ and carbonyl groups are known[16]. Thus, the addition of alkaline salt will diminish the
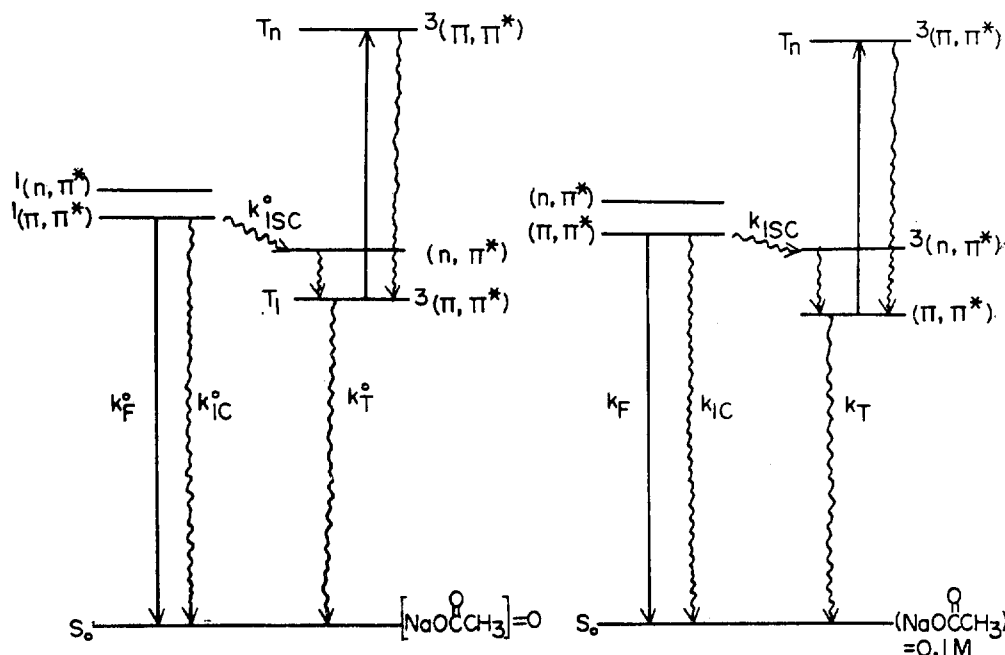

Fig. 5. The Jablonski diagram for *trans*-bispyrazyl ethylene in ethanol at 77 °K.

fluorescence intensity of BPE if (n, π^*) state is fluorescent. *Fig.* 4 shows alkaline salt effects on fluorescence of *trans*-BPE. Sodium acetate enhances the fluorescence of *trans*-BPE indicating that the lowest and fluorescent excited state is $(\pi, \pi^*)^1$ state. A blue shift of the (n, π^*) state as a result of $\equiv$N:—cation coordination complexes widens the gap between the lowest $(\pi, \pi^*)^1$ and imbedded $(n, \pi^*)^1$ state as shown in *Fig.* 5 or increases (π, π^*) character in the lowest excited state. This also explains the unusual wavelength effect on the fluorescence quantum yield. Shorter wavelength radiation (313 nm) produces the excited state with more $(n, \pi^*)^1$ character which can undergo intersystem crossing to the T_1 state in competition with internal conversion and result, therefore, in a lower Φ_F compared to longer wavelength radiation[17] (366 nm).

cis-BPE is not fluorescent. Neither *trans* nor *cis*-BPE is phosphorescent indicating efficient intersystem crossing from T_1 to S_0.

ACKLNOWLEDGEMENT

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