

## 트랜스-1, 2-비스피라질에틸렌에 대한 분광학적 연구

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## Spectroscopic Studies of *trans*-1, 2-Bispyrazylethylene

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**요 약.** Stilbene 유도체인 *trans*-1, 2-bispyrazylethylene에 대한 분광학적 연구를 행하였다. 보통의 자외선 흡수스펙트럼에서는  $n \rightarrow \pi^*$  흡수밴드는 에너지가 비슷한  $\pi \rightarrow \pi^*$  흡수밴드에 가려져서 나타나지 않는데 2차 미분 스펙트럼과 저온(77°K)에서의 스펙트럼으로 부터  $n \rightarrow \pi^*$  흡수 밴드를 확인할 수가 있었다. 또한  $\pi \rightarrow \pi^*$  흡수밴드들의 전이에너지를 PPP-SCF-CI MO 방법으로 계산한 결과 스펙트럼에서 얻은 값과 잘 일치했다.

형광스펙트럼, 형광편광스펙트럼, 그리고 PPP-SCF-CI MO 방법에 의한 계산으로부터 형광을 내는 상태는  $^1(\pi, \pi^*)$  상태임을 알 수가 있었으며 이것은 형광에 대한 alkaline salt effect의 결과와 일치한다.

**ABSTRACT.** Spectroscopic studies of *trans*-1, 2-bispyrazylethylene (BPE), one of the stilbene analogues, were carried out. In normal UV spectra, a distinct  $n \rightarrow \pi^*$  absorption band is missing because of a strong, nearly isoenergetic  $\pi \rightarrow \pi^*$  absorption band. The second derivative and low temperature (77°K) UV absorption spectra were taken and  $n \rightarrow \pi^*$  absorption band was identified by these methods. The transition energies of  $\pi \rightarrow \pi^*$  transitions were calculated by Pariser-Parr-Pople (PPP)-SCF-CI MO method. The calculated values showed good agreement with the observed spectral data. Luminescence studies were also carried out at low temperature. From the fluorescence spectra, fluorescence polarization studies, and PPP-SCF-CI MO calculation, the fluorescent state was determined to be a singlet ( $\pi, \pi^*$ ) state. This conclusion is in good agreement with the results obtained from alkaline salt effects on the fluorescence of this compound.

### INTRODUCTION

The excited states of heteroaromatic compounds containing nitrogen show many phenomena to which have been paid much attention. But

there has been considerable confusion about many photophysical and photochemical processes in several nitrogen containing heterocyclics. Most of these arised from the fact that the study of these phenomena has been mainly spectroscopic

and ( $n, \pi^*$ ) states in many of these N-heterocyclics are difficult to identify from the spectra.

Synthesis and spectral properties of 1,2-bispyrazylethylene (BPE), one of the nitrogen containing stilbene analogues, were reported previously.<sup>1</sup> It was suggested that  $^1(n, \pi^*)$  state has about the same energy as  $^1(\pi, \pi^*)$  state and consequently extensive mixing between these two states results obscuring  $n \rightarrow \pi^*$  band. Pyrazine shows a distinct and exceptionally strong  $n \rightarrow \pi^*$  band at 328 nm ( $\epsilon$  1,040) and  $\pi \rightarrow \pi^*$  band at 260 nm ( $\epsilon$  5,600). Consequently *trans*-BPE was expected to show the well-defined stilbene energy levels plus a distinct ( $n, \pi^*$ ) state contrary to spectral observations. The excited states of *trans*-BPE are studied by low temperature UV-VIS and second derivative spectroscopy along with luminescence polarization and molecular orbital calculations.

## EXPERIMENTAL

**Materials.** *trans*-1,2-Bispyrazylethylene was synthesized by the method reported<sup>1</sup> and this was recrystallized from acetone immediately prior to use. Ethanol and *n*-hexane was purified by the method reported in the literature.

**Methods.** Ultraviolet-visible spectra were recorded on a Perkin-Elmer spectrophotometer Model 200 and second derivative spectra were obtained by attaching derivative recording 200-0507 accessory.

Fluorescence emission, excitation, and polarization spectra were recorded on Aminco-Bowman Spectrophotofluorometer.

Polarized excitation spectra were obtained by plotting the polarization degrees measured point by point with the fixed emission wavelength. Similarly, the polarized emission spectra were obtained with the fixed excitation wavelength. Degree of polarization ( $P$ ) at each wavelength of excitation or emission was calculated from

the following Azumi-McGlynn's formula,<sup>2</sup>

$$P = \frac{I_{EE} - I_{EB}(I_{BE}/I_{BB})}{I_{EE} + I_{EB}(I_{BE}/I_{BB})}$$

where subscript  $E$  and  $B$  refer to the vertical and horizontal orientations of the Glan-Thomson prism polarizers, respectively and the first and second letters in the pair of subscripts refer to the exciting and analyzing polarizer orientations, respectively.

Transition energies, oscillator strength, and polarization directions were calculated by the PPP (Pariser-Parr-Pople)-SCF-CI MO method.<sup>3</sup> The semi-empirical integrals used in computation are listed in Table 1.

The one-center repulsion integral,  $\langle rr/rr \rangle$ , was evaluated according to the Pariser-Parr approximation and the two-center integral,  $\langle rr/rs \rangle$ , was estimated by the Mataga-Nishimoto formula.<sup>4</sup>

## RESULTS AND DISCUSSION

One of the characteristics of UV-VIS absorption spectra, particularly in polar solvents, is the broad nature of the observed bands due to the overlap of many rotational, vibrational and electronic transitions. Precisions in quantitative and qualitative studies are limited by this phenomenon.

Many methods have been utilized to reduce the effective bandwidth of absorbing species in order to separate overlapping absorption bands. One of these methods is to obtain the spectra at low temperature, that is, cooling the sample to cryogenic temperature where vibrational and

Table 1. Semiempirical integrals (in eV) for PPP-SCF-CI MO calculations.

Atom	Ionization Potential ( $-W_{2p}$ )	$rr/rr$
C	11.16	11.13
N	14.20	12.34

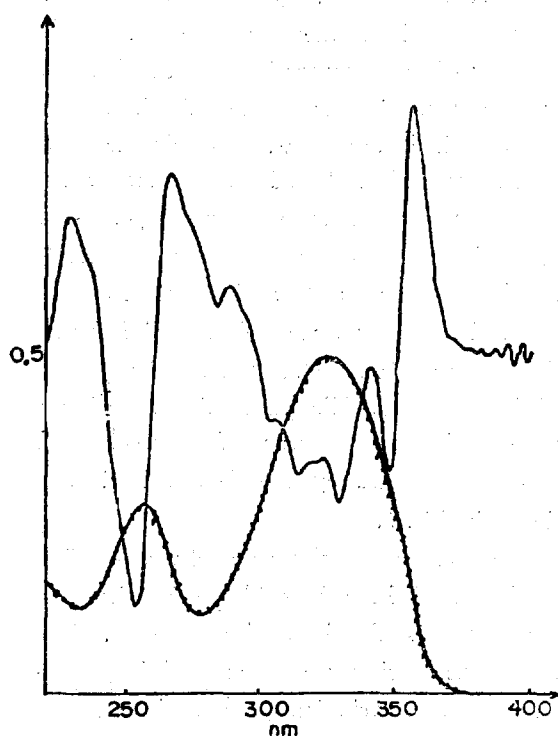


Fig. 1. Normal (····) and second derivative (—) UV spectrum of *trans*-BPE in ethanol.

rotational transitions are minimized. This method is very effective but low temperature spectra require sophisticated apparatus and time consuming procedures. Moreover, there is the possibility of introducing other effects such as molecular aggregation due to solidification of the sample.

Another method of increasing the resolution of the spectra is the derivative spectroscopy which is a relatively new analytical principle in spectroscopy.<sup>5</sup> A derivative spectrum is the graphic representation of the differential quotient,  $\frac{dA}{d\lambda}$  (for the first derivative) and  $\frac{d^2A}{d\lambda^2}$  (for the second derivative) over the wavelength range of interest, where  $A$  and  $\lambda$  mean absorbance and wavelength respectively. Higher derivatives are of lesser interest for normal use.

In the second derivative spectrum, the point

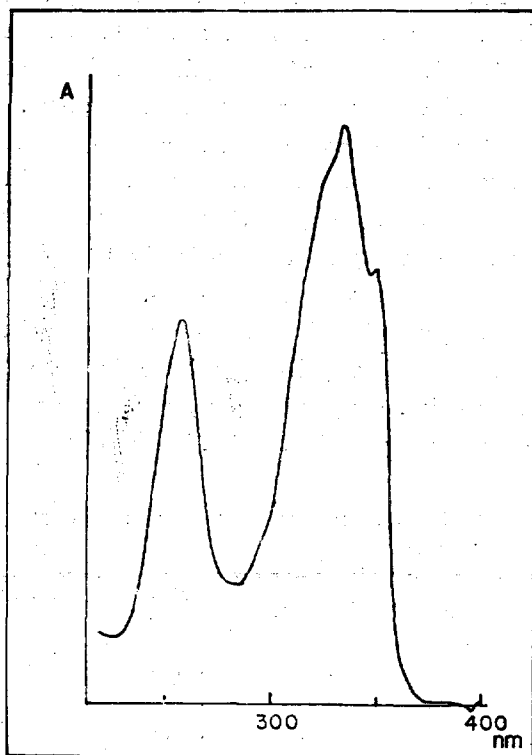


Fig. 2. UV spectrum of *trans*-BPE in ethanol at 77°K.

of inflection in the normal spectrum appears as maximum and the absorption maximum becomes a minimum.

The second derivative spectrum of BPE in ethanol solvent at room temperature is presented with a normal spectrum in Fig. 1. A new absorption band at 347 nm, possibly a  $n \rightarrow \pi^*$  band, is clearly shown along with  $\pi \rightarrow \pi^*$  B band at 329 nm in the second derivative spectrum. The same bands were observed in *n*-hexane solution. A low temperature (77°K) absorption spectrum of BPE was recorded in ethanol matrix and 347 nm band is again detected as shown in Fig. 2.

PPP-SCF-CI MO calculations on the  $\pi \rightarrow \pi^*$  transitions for *trans*-BPE is carried out and the results are compared with experimental observations as shown in Table 2. The calculated values

are in good agreement with the observed spectral data. It thus appears clear that the band at 347 nm is the  $n \rightarrow \pi^*$  absorption band which was hidden in the normal absorption spectra.

Most of the organic photochemical processes start from the lowest excited singlet and triplet states in condensed phase.<sup>6</sup> It is, therefore, one of the most important things in photochemistry to study the nature of these states.

The properties of the lowest excited singlet state are studied by fluorescence and fluorescence polarization. As previously reported, the fluorescence spectrum of *trans*-BPE in ethanol matrix

at 77 °K is broad with  $\lambda_{\max}$  at around 430 nm. Alkaline metal salt effects on the fluorescence intensity of the compound indicated that the fluorescent state is  $^1(\pi, \pi^*)$  state which is strongly mixed with  $^1(n, \pi^*)$  state. The vibronic interaction between  $^1(n, \pi^*)$  and  $^1(\pi, \pi^*)$  states are not uncommon in N-heteroaromatic compounds.<sup>7,8</sup> A small energy difference between  $^1(n, \pi^*)$  and  $^1(\pi, \pi^*)$  states and broad nature of absorption and emission spectra<sup>9,10</sup> of *trans*-BPE support the strong mixing of  $^1(n, \pi^*)$  and  $^1(\pi, \pi^*)$  states of the compound. Alkaline metal salts enhance the intensity of fluorescence of *trans*-BPE and this was explained by the Jablonski diagram shown in Fig. 3.

Table 2. Calculated and observed  $\pi \rightarrow \pi^*$  absorption maxima in BPE.

Transition <sup>a</sup>	$\lambda_{\max}$ (nm)	(Oscillator $f$ strength)	Observed $\lambda_{\max}$ <sup>b</sup>
7 8	326.84	.2215	324
7 10	247.46	.3425	258
6 8	228.20	.0178	—

<sup>a</sup> The first and last numbers represent indices of the closed shell and virtual orbitals, respectively, in the order of increasing orbital energy.

<sup>b</sup> *trans*-BPE in ethanol at room temperature.

The fluorescence polarization of *trans*-BPE is studied to reinforce the evidence that the fluorescent state is the lowest  $^1(\pi, \pi^*)$  state. The fluorescence excitation spectrum and the polarized fluorescence excitation spectrum of *trans*-BPE in ethanol matrix at 77 °K are shown in Fig. 4. The fluorescence and polarized fluorescence emission spectra of *trans*-BPE in ethanol at 77 °K are recorded in Fig. 5.

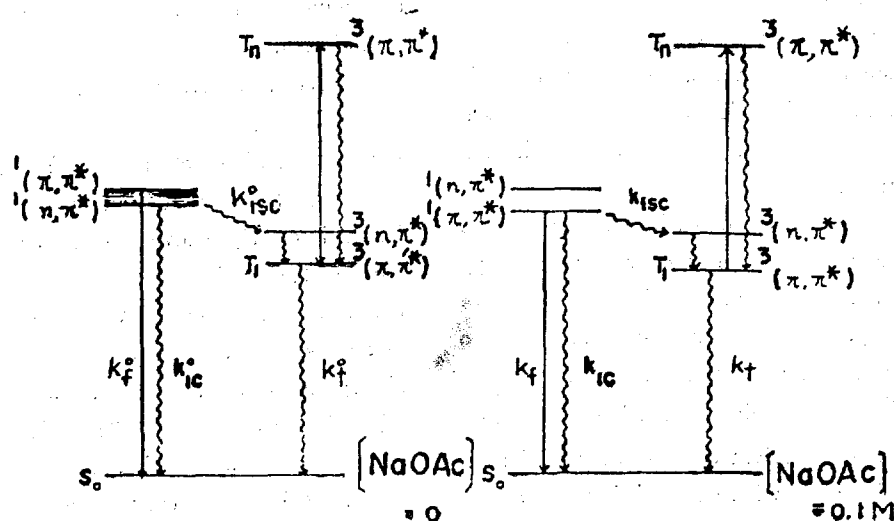


Fig. 3. The Jablonski diagram for *trans*-BPE in ethanol.

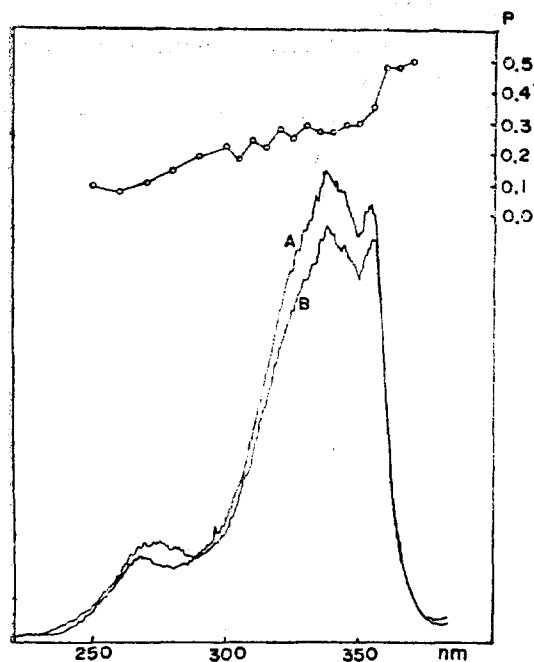


Fig. 4. Fluorescence excitation spectrum (uncorrected, A;  $\lambda_{em}=440$  nm, B;  $\lambda_{em}=400$  nm) and polarized fluorescence excitation spectrum of *trans*-BPE in ethanol at 77 °K.

In the excitation spectra, the degree of polarization,  $P$ , has positive values and approaches +0.5 at longer wavelength region. The fluorescence polarizations are also positive as shown in Fig. 5. The fluorescence polarization with respect to 340 nm excitation is less positive, and this is internally consistent with the polarized fluorescence excitation spectra.

Calculations of the polarization by PPP-SCF-CI MO method indicate that  $\pi \rightarrow \pi^*$  transition bands at 327 and 248 nm are polarized along the long axis of the molecule. On the basis of the positive values of polarization and PPP-SCF-CI MO calculations, it is, therefore, clear that the fluorescent state of *trans*-BPE is the singlet ( $\pi, \pi^*$ ) state.

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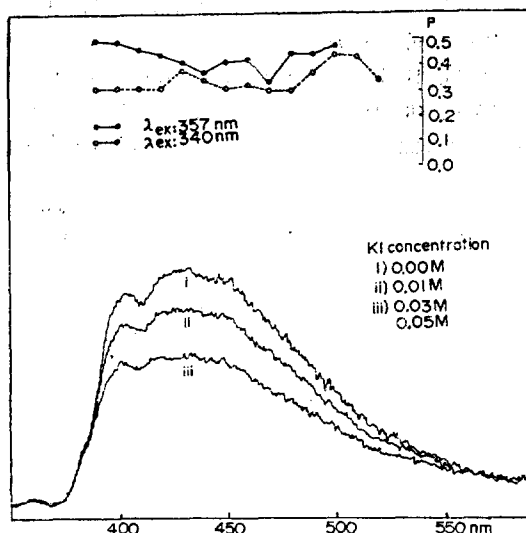


Fig. 5. Fluorescence and polarized emission spectrum of *trans*-BPE in ethanol at 77 °K. KI salt effect on the fluorescence is also shown.

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