

Figure 2. Photoreaction of thioxanthone with cyclohexene in dichloromethane.

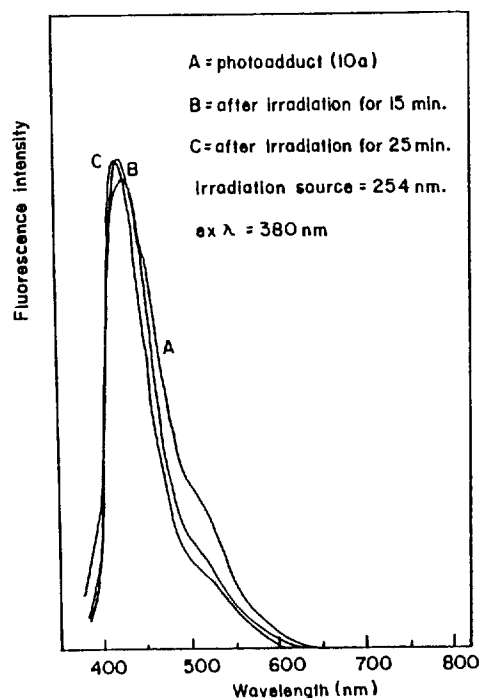


Figure 3. Photodecomposition of thioxanthone-cyclohexene photoadduct (10a) in dichloromethane.

anthrone also react with DPA to yield the same type of photoproducts, 8 and 9, respectively. These quinonoid compounds also react with cyclic olefins to give spiro-oxetanes.¹ Cyclic dienes, such as 1,5-cyclooctadiene, show closely parallel behaviour to that of cyclic olefins forming 1:1 adducts. When irradiated with 350 nm UV light, cyclohexene reacted with thioxanthone, anthrone, and anthraquinone to give 1:1 photoadducts, 10a, 10b, and 10c, respectively (Figure 2). The structure of the photoadducts (10a-10c) was identified by UV, IR, ¹H-NMR, and fluorescence spectra.

When irradiated with 254 nm UV light, the spiro-oxetanes decompose to the starting materials. It was analyzed by tlc, UV spectra, IR spectra, and fluorescence spectra (Figure 3). For example, 1:1 photoadduct (10a, A in Figure 3) of thioxanthone and cyclohexene was decomposed into the starting materials (C in Figure 3) by 254 nm UV light. Investigation of the mechanism and scope of the reaction is continuing.

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Theoretical Studies on 1,2-Bispyrazinylethylene

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A quantum mechanical studies on pyrazine and other diazines show that two orbitals with lone-pair characters are in general delocalized throughout the system. These two orbitals interact, depending on geometry to raise the energy of the highest filled "n" orbital and this in turn causes the red shifts in n- π^* transitions and leads to increase in the Van Vleck paramagnetic contributions.^{1,2}

The 1,2-bispyrazinylethylene(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 would therefore enrich the photochemistry of the stilbene to the considerable extent. The (n, π^*) and (π , π^*) excited singlet states often lead to different reaction paths. Since the character of (n, π^*) and (π , π^*) states are quite different.³ In this system, ¹(n, π^*) state has about the same energy as ¹(π , π^*) state has about the same energy as ¹(π , π^*) state and consequently extensive mixing between these two states results in obscuring the (n, π^*) band.⁴ It is clear the EHT calculation⁵

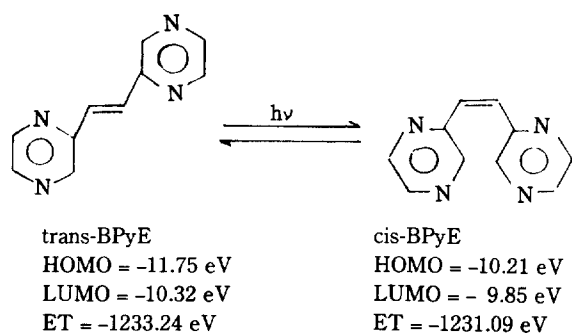


Figure 1. Calculated frontier orbital energies and total energies by EHT.

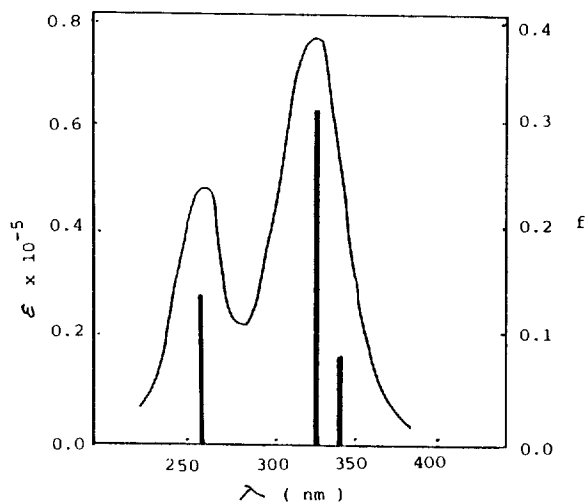


Figure 2. Calculated absorption Spectrum of trans-bispyrazinylethylene by PPP-SCF-CI (— experimental, — calculated).

predicts the *trans*-bispyrazinylethylene (BPyE) is more stable by some 2.15 eV than the corresponding *cis*-BPyE (Figure 1).

The spectral data and photoreactivity of the bispyrazinylethylene are compared with the results obtained from the oscillator calculation. The π - π^* transitions were calculated by the PPP-SCF-CI MO, configuration analysis.⁶ The two center electron repulsion integrals are estimated according to the Mataga and Nishimoto formula.^{7,8} The SCF CI wave functions of the molecule can be expressed in terms of the corresponding wave functions of reference orbitals by using configuration analysis method. Details of the configurational analysis procedure are reported elsewhere.⁹ Oscillator strength, f , is used quantitatively to indicate the relative intensity of various transitions, primarily in the visible, UV and vacuum UV region. Pyrazine shows a distinct and exceptionally strong n - π^* band at 328 nm ($\epsilon = 1,040$) and a π - π^* band at 260 nm ($\epsilon = 5,600$). Consequently bispyrazinylethylene was expected to show the well-defined stilbene energy levels plus a distinct (n, π^*) state contrary to spectral observations. Figures 2 and 3 compare the experimental and theoretical (PPP-CI) spectra for π - π^* transitions in 1,2-bispyrazinylethylene. The first maxima, occurring at 326 nm for *trans*-bispyrazinylethylene and at 295 nm for *cis*-bispyrazinylethylene, are assigned as π - π^* band because of their large molar absorptivities and slight spectral change with solvent varia-

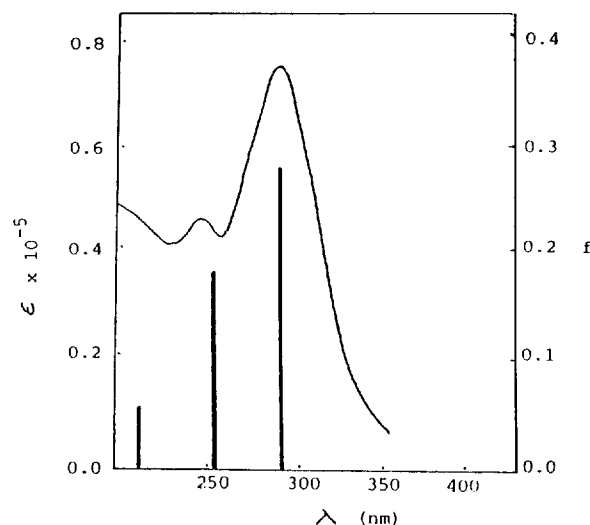


Figure 3. Calculated absorption spectrum of *cis*-bispyrazinylethylene by PPP-SCF-CI (— experimental, — calculated).

tions. The calculated π - π^* transition energies are in reasonably good agreement with the experimental values.⁴ It appears clear that the band at 347 nm for *trans*-BPyE is the n - π^* absorption band which is hidden in the normal absorption spectra. Most of the organic photo processes are from the lowest excited singlet and triplet states in condensed phase.¹⁰

The polarization by PPP-SCF-CI calculation indicate that π - π^* transition bands at 326 for *trans*-BPyE and for *cis*-BPyE 248 nm are polarized along the axis of the molecule. On the basis of the positive values of polarization and molecular orbital calculations, it is, therefore, shown that the fluorescent state of *trans*-BPyE is the singlet (n, π^*) state.

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