

containing potassium chromate in aqueous potassium carbonate. This filter solution transmits radiation only from 3000–3250 Å and therefore isolates the 3130-Å mercury line.

**Procedures.** Dimerization quantum yields were determined by parallel irradiation of deaerated samples contained in sealed 13 × 100 Pyrex tubes. Dimer yields at various enone concentrations were determined by glpc analysis. They never exceeded 5% total conversion. The (area ratio)/(mole ratio) response of the FID detectors was calibrated with known mixtures of dimers and internal standards. It was assumed that the HH and HT dimers produce the same response.

Quantum yields for the sensitized isomerization of pentadiene were determined by parallel irradiation of deaerated samples containing 0.5 M ketone and various concentrations of *cis*-1,3-pentadiene. With acetophenone as sensitizer,  $\Phi_{c \rightarrow t}$  equals 0.56;<sup>12</sup> this system was used as an actinometer. Conversions ranged from 3 to 15%. Quantum yields were corrected for back reaction by the following expression, where *F* is the per cent *trans*-diene

$$F_{\text{corr}} = 0.56 \ln \left( \frac{0.56}{0.56 - F_{\text{obsd}}} \right)$$

Quenching studies on the dimerizations were performed by parallel irradiation of deaerated samples containing given concentrations of enone and internal standard and varying concentrations of pentadiene or cyclohexadiene.

Photostationary states for pentadiene were determined by irradiation of two sets of solutions, one initially 60:40 and one 50:50, until no further change in the *trans/cis* ratio occurred when approached from either direction.

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## Radiationless Processes in the Photochemistry of Stilbazoles and 1,2-Bispyridylethylenes<sup>1</sup>

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**Abstract:** Reactions of excited states of several stilbazoles and 1,2-bispyridylethylenes have been studied. Quantum efficiencies of fluorescence, intersystem crossing, and internal conversion to the ground state have been determined. Rate constants for these processes were calculated by a comparison of the quantum yields, using the rate constants for fluorescence calculated from absorption spectra. Rate constants for intersystem crossing for several of the azastilbenes (assuming a triplet mechanism for the direct isomerization) are calculated to be quite high even though quantum efficiencies are low. Internal conversion from the excited singlet to the ground state not involving geometric change is shown to be an important process for 2-stilbazole and all of the bispyridylethylenes in contrast to the behavior of excited singlets of stilbene. In this respect the behavior of the azastilbenes resembles that of pyridine, the diazines and other N-heteroaromatics in which radiationless deactivation of the singlet state is the major process. Rates of the various deactivation processes depend on nitrogen location. Possible mechanisms for the enhanced internal conversion processes are discussed.

Phenomena regarding excited states of nitrogen heterocyclic compounds have received much attention. Interest in these compounds has been aroused in part by theoretical studies and in part by the presence of these structures in biologically important systems. The rich array of  $n-\pi^*$  and  $\pi-\pi^*$  states in these compounds should provide for a variety of interesting physical and chemical conversion processes. While chemical reactions have been observed in a few nitrogen heterocyclics, a more frequently encountered phenomenon for simpler azines is a high rate and efficiency of radiationless deactivation. Until rather recently, there has been considerable confusion regarding the importance of fluorescence, intersystem crossing, and phosphorescence in several N-heterocyclics. Much of the uncertainty is due to the fact that characterization of excited states of these compounds has been chiefly spectroscopic. Emission spectra are usually weak and reliable quantum efficiencies are difficult to obtain. An interesting example concerns the diazines, which have been the subject of extensive investigation.<sup>3</sup> Based on theoretical considera-

tions, El-Sayed<sup>4</sup> concluded that intersystem crossing between orbitally different states should proceed much more rapidly than transitions between states of the same type. Thus, fluorescence in the diazines, such as pyrazine, was at first believed to be weak due to efficient intersystem crossing.<sup>4,5</sup> Extensive investigations by Cohen and Goodman<sup>6</sup> using piperylene sensitization<sup>7</sup> method for determining intersystem crossing efficiencies indicate that most of the quanta delivered to the various diazines are degraded by radiationless decay of the singlet. Other studies<sup>8</sup> suggest that efficient internal conversion processes may deactivate singlets of other azines although theoretical considerations<sup>9</sup> predict little differences in rates of  $S_1-S_0$  internal conversion for aromatics and N-heteroaromatics.

(3) For a review see K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectry.*, **22**, 125 (1967).

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

(5) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1959); L. Goodman, *J. Mol. Spectry.*, **6**, 109 (1961).

(6) B. J. Cohen and L. Goodman, *J. Chem. Phys.*, **46**, 713 (1967), and references therein.

(7) A. A. Lamola and G. S. Hammond, *ibid.*, **43**, 2129 (1965).

(8) J. Lemaire, *J. Phys. Chem.*, **71**, 612 (1967).

(9) J. P. Byrne, E. F. McCoy, and I. G. Ross, *Australian J. Chem.*, **18**, 1589 (1965).

(1) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract PHYS-171.

(2) National Aeronautics and Space Administration Predoctoral Fellow, 1966–present.

Our work in this area deals with the photochemical behavior of the stilbazoles (styrylpyridines) and 1,2-bispyridylethylenes, nitrogen analogs of stilbene. These compounds are attractive candidates for study since, to a first approximation, they contain both the well-defined stilbene energy levels plus  $n-\pi^*$  states. Though there are still problems concerning mechanistic details of the photochemistry of stilbene,<sup>10</sup> the reactivity of singlet and triplet states of stilbene and many substituted stilbenes has been well characterized. Therefore, it should be possible to gain a great deal of information by evaluating the perturbations introduced by nitrogen substitution. Previous studies of the stilbazoles have shown in fact that both *cis-trans* isomerization<sup>14</sup> and cyclization reactions occur.<sup>15,16</sup> In the present paper we report studies of both direct and sensitized isomerization which reveal that excited states of the aza-substituted stilbenes, unlike those of other substituted stilbenes, decay in part *via* paths which maintain geometric integrity.

### Experimental Section

**Materials.** *trans* isomers of the nitrogen-containing olefins with the exception of 3-stilbazole and 3,3'-BPE were prepared by the condensation of  $\alpha$ - or  $\gamma$ -picoline with an appropriate aldehyde.<sup>17,18</sup> The procedure was to reflux for approximately 10 hr a solution of 20 g of aldehyde and 80 g of picoline in 100 ml of acetic anhydride. The reaction mixture was concentrated on a rotary evaporator and the residue was distilled under reduced pressure. The olefins distilled as yellow oils which solidified upon standing. Purification was achieved by several recrystallizations from hexane or benzene. Where necessary, preparative vapor phase chromatography was used in the purifications. 3-Stilbazole and 3,3'-BPE were prepared by the method of Clark, *et al.*<sup>19</sup>

*cis*-4,4'-BPE was prepared by the preparative-scale benzil-sensitized photoisomerization of *trans*-4,4'-BPE. *cis*-4,4'-BPE was separated by chromatography over alumina, eluting with 5% benzene in hexane. Purification was accomplished by several recrystallizations from hexane.

*Anal.* Calcd for  $C_{12}H_{10}N_2$ : C, 79.13; H, 5.49. Found: C, 79.08; H, 5.42.

Other *cis* olefins were prepared from *trans* isomers either by benzil sensitization or by direct irradiation.<sup>20</sup> Purification was by preparative vapor phase chromatography.

Purity of the olefins was determined by vapor phase chromatography to be greater than 99.9% except where indicated otherwise.

Azulene (J. T. Baker) was vacuum sublimed twice before use. Benzophenone and benzene were zone refined from James Hinton. Other solvents were spectral quality and were distilled before use. Trichloroacetic acid was B & A reagent grade and was used as obtained.

**Spectra.** Absorption spectra were recorded on either a Unicam or a Cary Model 14 recording spectrophotometer. Emission spectra were recorded on an Aminco Bowman spectrophotometer. Relative intensities of fluorescence were determined for very dilute (OD 0.55) solutions. Samples were degassed either by bubbling with argon or by the freeze-pump-thaw method. Similar results were obtained by both techniques. No correction was made for

photomultiplier tube response since emission from all compounds occurred at approximately the same wavelength. Quantum yields were calculated from relative intensities and the reported quantum yield of fluorescence of stilbene. The primary source of error in these determinations is the low intensity of fluorescence for most of the stilbazoles and bispyridylethylenes. Precision is within 50% for most olefins, slightly better for 3-stilbazole and 3,3'-BPE, but poorer for 4,4'-BPE.

**Isomerization.** Quantum yields for isomerization were obtained by irradiating sealed, degassed solutions in Pyrex ampoules. Degassing was by three freeze-pump-thaw cycles. Irradiations were by a medium-pressure mercury lamp in a merry-go-round apparatus.<sup>11</sup> Mercury emission lines of 3130 and 3660 Å were isolated by filters for direct and sensitized isomerizations, respectively. The following filters were used: 3130 Å, 7-54 Corning glass filter and a 0.7-cm path, 0.0025 M  $K_2CrO_4$  in 1%  $Na_2CO_3$ ; 3660 Å, Corning glass filters 0-52 and 7-37. Ferric oxalate actinometry was used to monitor the intensity of the exciting light.<sup>21</sup> Analysis was by vapor phase chromatography on either a Perkin-Elmer 881 or F & M Model 5754, both equipped with flame ionization detectors. Columns which proved to be most useful were the following: 8 ft, 1/8 in., 5% SE 30 on Chromosorb G; 8 ft, 1/8 in., 10% W98 on Chromosorb G; 8 ft, 1/8 in., 5% fluorosilicate (FS 1265) on Chromosorb G.

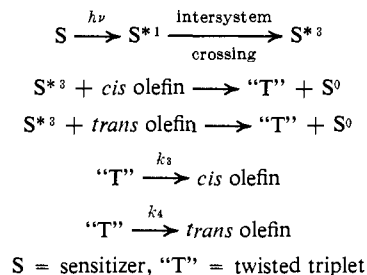
In determination of quantum yields all isomerizations were carried to very low conversions (1-5%) to prevent appreciable back-reaction.

### Results

The photochemistry of *trans* isomers of the 1,2-bispyridylethylenes (hereafter referred to as BPE's with prefixing numbers denoting nitrogen position relative to the double bond) and stilbazoles is characterized by three measurable phenomena. These are sensitized (triplet state) isomerization, isomerization on direct irradiation, and fluorescence. For clarity they are discussed separately.

**Sensitized Reactions.** Triplet states of olefins, particularly those of stilbene and related compounds, have been the subject of much investigation.<sup>11-13,22</sup> The photochemistry and kinetics for several olefins can be explained satisfactorily by a mechanism whereby *cis* or *trans* triplets decay rapidly and efficiently to a common twisted form of lower energy. It is likely that excited triplet- and ground-state potential surfaces cross at some point near the 90° or twisted form.<sup>11,23</sup> The simplest situation in a sensitized reaction can be described using Scheme I. Where the sensitizer triplet energy is high

#### Scheme I



enough so that energy transfer to both isomers is diffusion controlled and the olefin concentration sufficient to capture all sensitizer triplets, the following relationships should be observed

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(22) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962).

(23) P. Borrell and H. H. Greenwood, *Proc. Roy. Soc. (London)*, **A298**, 453 (1967).

(10) See, for example, ref 11, 12, and 13 and later discussion.

(11) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(12) (a) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 3907 (1968); (b) *ibid.*, **90**, 12 (1968); (c) *ibid.*, **89**, 4814 (1967).

(13) (a) J. Saktiel, *et al.*, *ibid.*, **88**, 2336 (1966); (b) *ibid.*, **89**, 1037 (1967); (c) *ibid.*, **90**, 6394 (1968); (d) *ibid.*, **90**, 4759 (1968).

(14) P. Bortulus, G. Cauzzo, U. Mazzucato, and G. Galiazzi, *Z. Phys. Chem. (Frankfurt-am-Main)*, **51**, 264 (1966).

(15) C. E. Loader and C. J. Timmons, *J. Chem. Soc.*, **C**, 1078 (1966).

(16) H. H. Perkampus and P. Senger, *Ber. Bunsenges. Phys. Chem.*, **67**, 876 (1963).

(17) M.-C. Chiang and W. H. Hartung, *J. Org. Chem.*, **10**, 21 (1945).

(18) Samples of commercially available (Aldrich) bispyridylethylenes were purified as described above.

(19) F. Clarke, G. A. Felock, G. B. Silverman, and C. M. Watrick, *J. Org. Chem.*, **27**, 533 (1962).

(20) We thank Messrs. P. D. Wildes and Y. J. Lee for preparing *cis*-2-stilbazole and *cis*-4-stilbazole, respectively. The only detectable impurity in each was approximately 3% of the *trans* isomer.

$$\phi_{c \rightarrow t} = \phi_{S,isc} \frac{k_4}{k_3 + k_4}$$

$$\phi_{t \rightarrow c} = \phi_{S,isc} \frac{k_3}{k_3 + k_4}$$

$$\text{stationary state, fraction } cis = \frac{k_3}{k_3 + k_4}$$

$$\phi_{c \rightarrow t} + \phi_{t \rightarrow c} = \phi_{S,isc}$$

where  $\phi_{c \rightarrow t}$  = initial quantum yield of pure *cis*  $\rightarrow$  *trans*;  $\phi_{S,isc}$  = sensitizer intersystem crossing efficiency. For the case where benzophenone (a high-energy sensitizer,  $\phi_{S,isc} = 1$ ) is used as a sensitizer, the sum of the initial quantum yields should be close to unity and the value of  $\phi_{t \rightarrow c}$  should be predicted by the stationary-state composition. This is the case for several stilbene derivatives and some conjugated dienes.

All of the stilbazoles and bispyridylethylenes undergo sensitized *cis*-*trans* isomerizations. Benzophenone-sensitized stationary states for all of the nitrogen compounds except 2,2'-BPE are close to 60% *cis*, the value obtained for stilbene<sup>11</sup> (Table I). We find that benzil (triplet energy 53 kcal/mol)<sup>24</sup> gives *cis*-rich stationary states (80-99%) for all of the stilbazoles and bispyridylethylenes. These results suggest that triplet energies for the *cis* and *trans* isomers are similar to those of stilbene.<sup>25</sup>

**Table I.** Benzophenone-Sensitized Isomerization<sup>a</sup> of Stilbazoles and Bispyridylethylenes

Compound	$\phi_{t \rightarrow c}$	$\phi_{c \rightarrow t}$	Stationary state, % <i>cis</i>
Stilbene <sup>b</sup>	0.5	0.41	60
1,2-Diphenylpropene <sup>b</sup>	0.54	0.44	55
2-Stilbazole	0.44 $\pm$ 0.02	0.34	52.8 $\pm$ 0.9 <sup>c</sup>
3-Stilbazole	0.44		60.7 $\pm$ 0.9
4-Stilbazole	0.40	0.35	50.3 $\pm$ 1.1 <sup>c</sup>
2,2'-BPE	0.13	0.18	32.4 $\pm$ 0.5
2,3'-BPE	0.42		59.1 $\pm$ 1.1
2,4'-BPE	0.22		66.0 $\pm$ 1.0
3,3'-BPE	0.48	0.22	64.0 $\pm$ 0.3
3,4'-BPE	0.44		53.3 $\pm$ 0.9
4,4'-BPE	0.39	0.21	58.3 $\pm$ 0.5

<sup>a</sup> Olefin concentration, 0.005 *M*; benzophenone, 0.05 *M*; solvent, benzene; temperature 25-30°. <sup>b</sup> Data from ref 11. <sup>c</sup> Olefin concentration 0.01 *M*.

Quantum yields for benzophenone-sensitized isomerization of bispyridylethylenes and stilbazoles are given in Table I. Table I indicates that all of the nitrogen compounds undergo *cis*-*trans* isomerization with relatively low efficiency. The values are considerably lower than those for stilbene and methylstilbene and the sum of the quantum yields,  $\phi_{c \rightarrow t} + \phi_{t \rightarrow c}$ , is less than unity. The values in Table I are uncorrected for back-reaction; however, since the experiments were taken to very low conversion in all cases, the standard back-reaction correction<sup>7</sup> raises none of the quantum efficiencies by more than 10%. According to the above-outlined scheme for sensitized isomerization, high-energy sensitizers should promote stationary states having *trans/cis* ratios

(24) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(25) Very weak singlet-triplet absorption spectra in 2-iodotoluene give triplet energies of ca. 50 kcal/mol for *trans*-4-stilbazole and *trans*-4,4'-BPE.

equal to  $\phi_{c \rightarrow t}/\phi_{t \rightarrow c}$ . Curiously, this is not the case for several of the compounds listed in Table I. Table II indicates that photostationary states for several of the compounds become *cis*-rich with decreasing olefin concentration and that except for the case of the 2,2'-BPE, the  $\phi_{c \rightarrow t}/\phi_{t \rightarrow c}$  ratios are close to the photostationary-state values for dilute solutions. Interestingly the change in stationary-state composition with olefin concentration is more pronounced for the nitrogen compounds than for stilbene.<sup>11,13c</sup>

**Table II.** Comparison of Quantum Yield and Photostationary-State Ratios in Benzophenone Sensitization Experiments<sup>a</sup>

Compound	$\phi_t/\phi_c$	( <i>t/c</i> ) <sub>ps</sub> , 0.01 <i>M</i>	( <i>t/c</i> ) <sub>ps</sub> , 0.001 <i>M</i>
2-Stilbazole	0.77	0.89 $\pm$ 0.04	0.72 $\pm$ 0.07
4-Stilbazole	0.88	0.99 $\pm$ 0.04	
2,2'-BPE	1.38	2.05 $\pm$ 0.07	1.47 $\pm$ 0.07
3,3'-BPE	0.46	0.65 $\pm$ 0.01	0.62 $\pm$ 0.02
4,4'-BPE	0.56	0.84 $\pm$ 0.02	0.57 $\pm$ 0.03

<sup>a</sup>  $\lambda = 3660$  nm; [benzophenone] = 0.05 *M*.

In studies with stilbene,<sup>11,13</sup> it was found that in addition to the twisted triplet, "T," a triplet having geometry similar to *trans*-stilbene had an appreciable lifetime and could be quenched selectively to *trans*-stilbene by added quenchers. Experiments with benzophenone as sensitizer and azulene as a quencher allowed estimation of the lifetime of the stilbene triplet.<sup>11</sup> We find that plots of *trans/cis* ratios in the stationary state vs. azulene concentration are linear (as is the case with stilbene). Values obtained for the slope to intercept ratios are listed in Table III. Relative lifetimes for the various compounds can be obtained using the decay ratio with the assumption that azulene quenches both stilbene and nitrogen compound triplets with the same quenching constant.

**Table III.** Azulene Effects on Benzophenone-Sensitized Photoisomerization<sup>a</sup>

Compound	Slope:intercept <sup>b</sup>	Estimate of rel Lifetime
Stilbene	120 <sup>c</sup>	1
2-Stilbazole	340	2.8
2,2'-BPE	810	9.7
2,3'-BPE	500	4.1
3,3'-BPE	290	2.2
4,4'-BPE	250	1.8

<sup>a</sup> At 3660 nm, olefin concentration 0.005 *M*. <sup>b</sup> From plots of (*t/c*)<sub>ss</sub> vs. [azulene]; photostationary states measured from both directions. <sup>c</sup> Data from ref 11.

In the studies of azulene quenching of stilbene isomerization,<sup>11,13</sup> it was found that only the *transoid* triplet was quenched, and that presumably all other bimolecular reactions of the triplet were rendered unimportant. Recently Salties<sup>13</sup> showed that for stilbene the ratio  $\phi_{c \rightarrow t}/\phi_{t \rightarrow c}$  in the presence of azulene agreed well with the ratio of the stationary-state concentrations of the isomers at the same azulene concentration. We have measured isomerization quantum yields for several of the nitrogen compounds and stilbene in the presence of azulene using solutions containing azulene, benzophenone, and 1,2-diphenylpropene (whose triplets are not quenched by azulene) as a standard.

Results of these experiments are listed in Table IV. There is good agreement between  $\phi_{c \rightarrow t}/\phi_{t \rightarrow c}$  and the *trans/cis* stationary-state value at the same azulene concentrations. In addition, for all of the compounds except 2,2'-BPE the sum of the quantum yields,  $\phi_{c \rightarrow t} + \phi_{t \rightarrow c}$  is unity, within experimental error.

**Table IV.** Effect of 0.01 *M* Azulene on Quantum Yields and Photostationary States in Benzophenone Photosensitization<sup>a</sup>

Compound	$\phi^b$	$\phi_t/\phi_c$	(t/c) <sub>ps</sub>
<i>cis</i> -Stilbene	0.67 ± 0.03	1.7	1.6 ± 0.1
<i>trans</i> -Stilbene	0.39 ± 0.05		
<i>cis</i> -2-Stilbazole	0.82		
<i>trans</i> -2-Stilbazole	0.25 ± 0.02	3.3	3.2 ± 0.1
<i>cis</i> -2,2'-BPE	0.66		
<i>trans</i> -2,2'-BPE	0.07	9.4	13.4 ± 0.1
<i>cis</i> -4,4'-BPE	0.60 ± 0.07		
<i>trans</i> -4,4'-BPE	0.34 ± 0.03	1.8	2.0 ± 0.1

<sup>a</sup> Quantum yields measured by irradiating solutions containing benzophenone, 0.05 *M*: azulene, 0.01 *M*: olefin 0.005 *M*. <sup>b</sup> *trans*-1,2-Diphenylpropene ( $\Phi_e = 0.55$ ) solutions with same concentrations of azulene and benzophenone were used as internal actinometers in order to eliminate effects of internal filtering and competitive deactivation of the sensitizer by azulene. Therefore, the tabulated values are defined as follows:  $\Phi = (\text{rate of isomerization})/(\text{rate of formation of excited olefin})$ .

**Direct Reactions.** Reactions of excited singlet states of the stilbenes have been well studied.<sup>11,12</sup> The principal means of deactivation of the lowest excited singlet state at room temperature is isomerization. For *trans*-stilbene the only other paths for deactivation are radiationless decay and fluorescence. The former is apparently unimportant;<sup>13</sup> the latter deactivates about 5% of the excited singlets. Ultraviolet spectra of *trans* isomers of the stilbazoles and bispyridylethylenes are similar to those of the stilbenes. In view of our finding reasonably efficient sensitized isomerization we expected to observe similarities in the direct reaction. To our considerable surprise we found that 4,4'-BPE undergoes very inefficient isomerization on direct irradiation.<sup>26</sup> The quantum yield is only 0.003, more than two orders of magnitude lower than that for stilbene. The isomerization proved to be nearly independent of solvent and showed no activation energy in the range 20–50°. Upon further examination we find that initial quantum yields for direct isomerization for all of the bispyridylethylenes are quite low compared to stilbene. The values (Table V) range from about one-third to two orders of magnitude lower. The stilbazoles, which contain only one nitrogen, isomerize much more efficiently. In each case no product other than the *cis* isomer builds up on moderate exposure. Upon long irradiation, considerably longer than that required to reach a stationary state, new products can be detected. These include phenanthrene derivatives as well as other products of undetermined structure. Studies with 4,4'-BPE, which shows the lowest efficiency of isomerization, indicate that solvent produces little or no effect on these phenomena.<sup>27</sup>  $\phi_{t \rightarrow c}$  remained nearly constant in ben-

(26) D. G. Whitten and M. T. McCall, *Tetrahedron Letters*, 2755 (1968).

(27) However, recent experiments indicate that there is a sharp increase ( $\Phi \sim 0.3$ ) in the quantum yield of isomerization of *trans*-4,4'-BPE when irradiated in 30% water in acetonitrile. Irradiation of *N,N*-dimethylformamide or ethanol solutions resulted in formation of small amounts of unidentified products which subsequently sensitized isomerization.

**Table V.** Initial Quantum Yields for Direct Isomerization and Intersystem Crossing of the Stilbazoles and Bispyridylethylenes

Compound	$\phi_{t \rightarrow c}^{a,b}$	$\phi_{isc}^c$
Stilbene <sup>d</sup>	0.48	0.95
2-Stilbazole	0.25	0.57
3-Stilbazole	0.43	0.97
4-Stilbazole	0.37	0.93
2,2'-BPE	0.01	0.08
2,3'-BPE	0.12	0.3
2,4'-BPE	0.07	0.32
3,3'-BPE	0.08	0.17
3,4'-BPE	0.09	0.20
4,4'-BPE	0.003	0.008

<sup>a</sup> Benzene solutions, olefin concentration 0.005 *M*;  $\lambda$  3130 nm. <sup>b</sup> Stationary states (although not determined precisely for all compounds) contain significant quantities of *cis* isomers at 3130 nm. For example, 4-stilbazole gives 88% *cis*, 4,4'-BPE gives >25% *cis*. <sup>c</sup> Calculated using eq 1. <sup>d</sup> Data from ref 11.

zene, methylcyclohexane, ethanol, and *N,N*-dimethylformamide.

We find that *cis* isomers of the stilbazoles and bispyridylethylenes also isomerize to *trans* with efficiencies much lower than *cis*-stilbene. For example,  $\phi_{c \rightarrow t}$  at 3130 Å in benzene for *cis*-4,4'-BPE is less than 0.01. The *cis-trans* isomerization is complicated by formation of yellow, fluorescent products which sensitize the isomerization. In nondegassed solutions significant amounts of phenanthrene derivatives are formed.<sup>15,16</sup>

There has been considerable controversy in recent years regarding the route of direct isomerization of the stilbenes. Hammond<sup>11</sup> and Fischer<sup>12</sup> suggest that isomerization proceeds *via* the lowest triplet state of the stilbenes. It has been suggested that the high efficiency of intersystem crossing demanded by a triplet mechanism is achieved by crossing from *S*<sub>1</sub> to a nearly isoenergetic *T*<sub>2</sub>.<sup>12,23</sup> Theoretical calculations<sup>23</sup> indicate that such a crossing is energetically possible. Saltiel,<sup>13</sup> on the basis of discrepancies between azulene quenching of the direct and sensitized isomerization and other experiments,<sup>13d</sup> suggests that the direct isomerization does not involve triplet states. Results of our studies do not allow us to distinguish between the two conflicting mechanisms in the case of the azastilbenes.<sup>28</sup> However, comparison of data for isomerization in direct and sensitized reactions does allow us to calculate *maximum* efficiencies for intersystem crossing. These *maximum* efficiencies (Table V), calculated by eq 1, are very low in

$$\phi_{isc} = \frac{\phi_{t \rightarrow c}(\text{direct})}{\phi_{t \rightarrow c}(\text{sensitized})} \quad (1)$$

several cases due to the striking contrast between direct and sensitized isomerization efficiencies. Table V indicates that only two of the azastilbenes studied, 3-stilbazole and 4-stilbazole, have crossing efficiencies approaching unity.

**Fluorescence Studies.** Ultraviolet spectra of *trans* and *cis* isomers of the stilbazoles and bispyridylethylenes are similar to those of the stilbenes. Figure 1 compares *trans* isomers of stilbene and 4,4'-BPE. In no case is there any sign of *n*- $\pi^*$  transitions. For the various *trans* isomers, calculated rates<sup>30</sup> of fluorescence

(28) Extinction coefficient corrected stationary states in direct isomerization have been found to be nearly the same as high energy sensitized stationary states for several azastilbenes.<sup>14,29</sup>

(29) Y. J. Lee, M. T. McCall, and D. G. Whitten, unpublished results.

are within 20% of that calculated for *trans*-stilbene,  $4 \times 10^8 \text{ sec}^{-1}$ .<sup>22</sup> We find that all of the *trans* isomers fluoresce with a dispersion pattern similar to stilbene but that efficiencies are much lower (Figure 1). Quantum yields<sup>31</sup> measured in benzene and/or methylcyclohexane using stilbene as a standard are listed in Table VI. Isomers with nitrogen only in *meta* positions fluoresce more efficiently than *trans*-stilbene; all other azastilbenes fluoresce with significantly lower efficiency.

**Table VI.** Quantum Efficiencies for Fluorescence of *trans* Isomers of the Stilbazoles and Bispyridylethylenes

Compound	$\phi_f$
Stilbene	0.05 <sup>a</sup>
2-Stilbazole	0.003
3-Stilbazole	0.07
4-Stilbazole	0.005
2,2'-BPE	0.005
2,3'-BPE	0.007
2,4'-BPE	0.003
3,3'-BPE	0.13
3,4'-BPE	0.005
4,4'-BPE	0.0004

<sup>a</sup> Data from ref 12c.

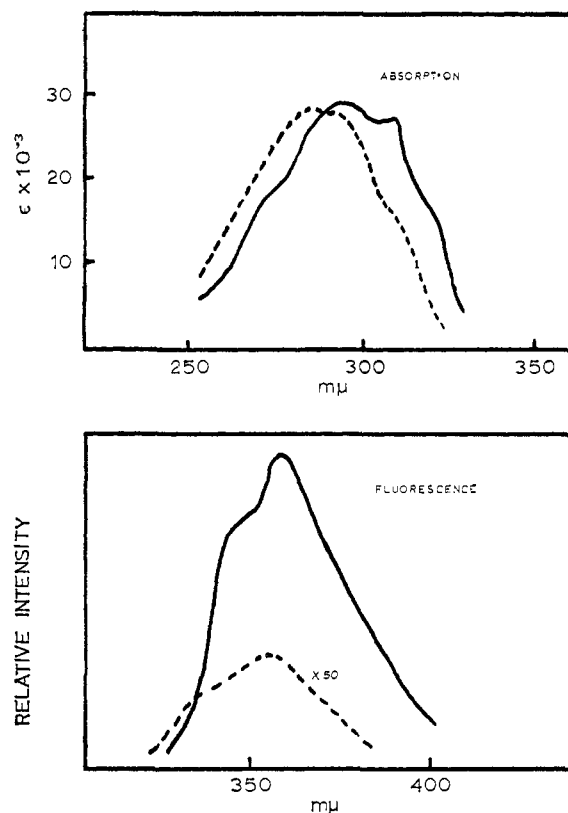
We have examined fluorescence for the nitrogen compounds in other media including ethanol and benzene or methylcyclohexane containing trichloroacetic acid. The change to ethanol produces only small effects on fluorescence. Both absorption and fluorescence spectra are red shifted in trichloroacetic acid-benzene for all compounds except the isomers with nitrogen only in *meta* positions. It is difficult to measure fluorescence efficiencies in trichloroacetic acid solutions; the peaks are broadened and occur at different frequencies than *trans*-stilbene fluorescence. However, the pattern observed for the stilbazoles<sup>14</sup> seems to hold for the bispyridylethylenes: 3,3'-BPE shows a slight increase while the other isomers show very slight decreases in fluorescence efficiencies. The fluorescence of *trans*-4,4'-BPE was examined at liquid nitrogen temperature in EPA. An increase in fluorescence efficiency was noted. However, the increase was less than a factor of 10.

## Discussion

Data in Tables I-VI indicate that deactivation of singlet and triplet states of the stilbazoles and bispyridylethylenes must include radiationless decay processes which proceed by paths not involving *cis-trans* isomerization. Results of the benzophenone sensitization studies indicate similarities between triplet states of the nitrogen compounds and stilbene but they also reveal significant differences. The result that concerns us most is the finding of lower than predicted (by the simple scheme) isomerization efficiencies in both directions. These reduced efficiencies clearly indicate that not all benzophenone triplets are effective in generating the twisted olefin triplet. The source of the inefficiency must therefore be either inefficient energy transfer from benzophenone to olefin or energy-degrading processes within the olefin triplet. The azulene results presented in Table IV suggest that the former is not the source of

(30) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 48.

(31) C. A. Parker and W. T. Rees, *Analyst*, **85**, 587 (1960).



**Figure 1.** Absorption and fluorescence spectra of stilbene, —, and 1,2-bis(4-pyridyl)ethylene, ---, in methylcyclohexane at 25°.

the inefficiency in most cases since the quantum efficiencies in the presence of the quencher sum to unity. Stilbene gives the same value within experimental error. Results in Table IV also suggest that potential surfaces for 2-stilbazole, 4,4'-BPE, and stilbene triplets are similar and that azulene quenches only the *transoid* forms. The lower than unity sum of quantum efficiencies for 2,2'-BPE may indicate inefficient energy transfer or it may reflect an altered potential surface where both *cis* and *trans* triplets are quenched by azulene.

The nature of energy-wasting steps within the olefin triplets is still not clear. It is probable that relaxation of planar triplets is competitive with decay of twisted forms. The concentration effects listed in Table II seem to indicate that some bimolecular quenching occurs. It is perhaps surprising that the lifetimes estimated by azulene quenching (Table III) are only slightly longer than that estimated for stilbene.

Although radiationless paths which maintain geometric integrity are important for the nitrogen compound triplet states, *cis-trans* isomerization provides the major route for deactivation. If we assume a triplet mechanism for isomerization in the direct reaction, we can obtain an energy balance for each compound. Table VII lists quanta not accounted for by fluorescence and intersystem crossing (isomerization) as radiationless decay. For 3- and 4-stilbazoles, excited singlet states of the *trans* isomers are almost completely accounted for by fluorescence and intersystem crossing (*cis-trans* isomerization) processes. However, for 2-stilbazole and all of the bispyridylethylenes major fractions of the excited singlet states are deactivated by some new process, not present in stilbene, which

**Table VII.** Quantum Yields and Calculated Rate Constants for Radiationless Decay and Calculated Rate Constants for Intersystem Crossing<sup>a</sup>

	$\phi_{RD}$	$k_{RD} \times 10^{-9},$ sec <sup>-1</sup>	$k_{isc} \times 10^{-9},$ sec <sup>-1</sup>
Stilbene			7.6
2-Stilbazole	0.43	57	77
3-Stilbazole			5.5
4-Stilbazole	0.07	5.6	74
2,2'-BPE	0.91	73	6.4
2,3'-BPE	0.70	40	17
2,4'-BPE	0.68	90	40
3,3'-BPE	0.70	2.2	0.52
3,4'-BPE	0.79	64	16
4,4'-BPE	0.99	800	8.0

<sup>a</sup> These values are calculated on the assumption that direct isomerization proceeds *via* a triplet mechanism.

amounts to a net internal conversion. Over 90% of the excited singlets of *trans*-4,4'-BPE and 2,2'-BPE decay by this route.

Approximate maximum rate constants for intersystem crossing and radiationless decay are also listed in Table VII. (An alternate interpretation of the rate constant  $k_{isc}$  is that it describes twisting about the central bond in S<sup>1</sup>.) These are calculated by comparing quantum yields for fluorescence, intersystem crossing, and radiationless decay with the calculated rate constants for fluorescence. Theoretical considerations<sup>4</sup> advanced by El-Sayed and others predict that intersystem crossing between  $\pi-\pi^*$  states and  $n-\pi^*$  states should proceed considerably faster than crossing between states of the same type. Though we see no evidence for low-lying  $n-\pi^*$  states in any of the stilbazoles or BPE's, it seems probable that crossing occurs from a lowest  $\pi-\pi^*$  singlet to an upper  $n-\pi^*$  triplet in many of these compounds. Interestingly, we find that intersystem crossing may be significantly faster in several of the compounds studied. Here again, the behavior of 3-stilbazole and 3,3'-BPE is significantly different from the other compounds in the series. Comparison of quantum efficiencies with rates of intersystem crossing for stilbene and the bispyridylethylenes provides a good example where efficiencies are a poor gauge of excited state reactivity.

The most surprising aspect of this study is our finding of enhanced radiationless processes in the azastilbenes. With the exception of a few 4-donor,4'-acceptor-disubstituted stilbenes,<sup>32</sup> none of the many stilbenes studied by Fischer and others<sup>12</sup> exhibit such phenomena. Spectral similarities between the bispyridylethylenes, stilbazoles, and stilbene and the lack of appreciable solvent effects in our studies make it clear that our results cannot be related to those obtained for 4-nitro-4'-methoxystilbene.<sup>12,32</sup> A complete explanation of our results is not warranted or possible at this time. However, since there has been much interest and speculation involving radiationless paths in N-heterocyclics, it seems worthwhile to discuss our results in terms of current ideas.

An obvious possibility for explaining the rapid rates of radiationless decay in the azastilbenes is the involvement of  $n-\pi^*$  states. There is increasing evidence that azaaromatics with lowest lying  $n-\pi^*$  singlet states have rapid rates of internal conversion. For example, pyri-

dine neither fluoresces nor phosphoresces.<sup>8</sup> Studies using pyridine as a sensitizer for the *cis-trans* isomerization of 2-butene indicate very low quantum efficiencies for formation of the pyridine triplet.<sup>8</sup> In spite of these results, no permanent or transient products have been detected for pyridine irradiated in the range 2600–2800 Å.<sup>33</sup> From studies of several azaaromatics, Hochstrasser and Marzzacco<sup>35</sup> have concluded that compounds which have either lowest  $n-\pi^*$  states, or lowest  $\pi-\pi^*$  states where  $n-\pi^*-\pi-\pi^*$  mixing occurs, show enhanced rates of radiationless decay. These authors have suggested very recently<sup>36</sup> that overlap or mixing of orbitally different states causes a severe breakdown of the Born-Oppenheimer approximation with consequential broadening of electronic spectra and acceleration of radiationless transitions. The spectral broadening is most prominent at low temperatures and in regions of  $n-\pi^*, \pi-\pi^*$  overlap. However, it has been suggested that even room temperature solution spectra of N-heteroaromatics such as pyridine or pyrazine show this effect.<sup>36</sup> As mentioned earlier, the stilbazoles and bispyridylethylenes have room temperature absorption spectra remarkably similar to that of *trans*-stilbene. No  $n-\pi^*$  transitions can be observed nor is there much broadening or loss of structure of the stilbene  $\pi-\pi^*$  spectrum. Of course, the solution spectrum of stilbene (Figure 1) has little structure to begin with. The only changes upon nitrogen substitution are small displacements and in some cases (most notably for 2-stilbazole and the bispyridylethylenes with a nitrogen in the 2 position) appearance of what seems to be a new maximum at *ca.* 2600–2700 Å.

The relative enhancement of radiationless decay on introduction of a second nitrogen into the stilbene manifold merits some comment. Note especially differences between 4-stilbazole and 4,4'-BPE and between 3-stilbazole and 3,3'-BPE in Tables V and VII. If  $n-\pi^*, \pi-\pi^*$  mixing or some other phenomenon involving  $n-\pi^*$  states is to account for the observed results, we must conclude that there is considerable interaction or cooperation between nitrogens in the bispyridylethylenes. More specifically, our results suggest that there may be significant separation of  $^1n-\pi^*$  states for the bispyridylethylenes so that the lower energy state in compounds such as 4,4'-BPE causes much greater perturbations. Both experimental and theoretical studies suggest that the  $n \rightarrow \pi^*$  transitions in pyrazine are little separated (*ca.* 400 cm<sup>-1</sup>) and that the falloff as the nitrogen separation increases from pyridazine to pyrazine is sharp.<sup>37</sup> Recent calculations, however, suggest both that nitrogen "lone pairs" in N-heteroaromatics are considerably delocalized<sup>38</sup> and that separation of the symmetry orbitals in compounds such as pyrazine may be considerably greater (as much as 1 eV or more) than was originally suspected.<sup>39,40</sup> Our results seem to reinforce these recent assertions.

(33) Results cited in ref 88 of ref 34.

(34) D. Phillips, J. Lemaire, C. S. Burton, and W. A. Noyes, Jr., *Advan. Photochem.*, **4**, 329 (1968).

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

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

(38) R. Hoffman, *ibid.*, **40**, 2745 (1964).

(39) E. Clementi, *ibid.*, **46**, 4731, 4737 (1967).

(40) J. L. Whitten, unpublished results.

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

There is increasing evidence that aromatic hydrocarbons, such as benzene, as well as many other types of compounds may degrade excitation energy *via* decay to an unstable (ground state) isomer which decays rapidly back to the starting material.<sup>41</sup> While evidence regarding this as a general route for internal conversion is rather limited, such isomers have been identified in several cases where energy balances could not be obtained.<sup>42</sup> This mechanism is attractive since it satisfies several existing theories regarding radiationless decay. Studies with pyrazine suggest that isomerization may be important in nitrogen compounds. Pyrazine and sub-

stituted pyrazines rearrange to the corresponding pyrimidines, presumably *via* benzvalene or prismane valence tautomers.<sup>43</sup> To date we have been unable to detect valence tautomers as intermediates or products in the photochemistry of the stilbazoles or bispyridylethylenes. We are currently pursuing experiments to test the possibility that enhanced radiationless decay proceeds *via* isomer formation.

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(41) For a review on this subject see ref 34.  
(42) L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **89**, 1030 (1967); K. E. Wilzbach and L. Kaplan, *ibid.*, **89**, 1031 (1967).

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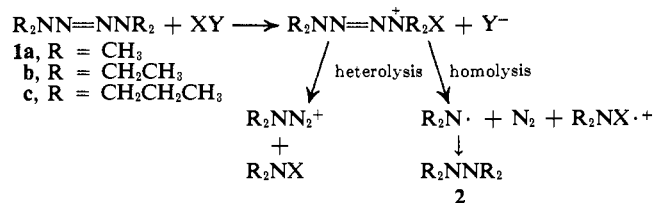
## Radicals from the Acid-Catalyzed Decomposition of 2-Tetrazenes

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**Abstract:** The radical products of acid- or anhydride-catalyzed tetramethyl-2-tetrazene (**1a**) decomposition are **1a**<sup>·+</sup> and tetramethylhydrazine radical cation, observed by esr. In solvents which give polyhalomethyl radicals upon halogen abstraction, a transient radical is formed in **1** decompositions; esr splittings show it contains the "CH<sub>2</sub>NCH<sub>3</sub>" fragment and the solvent radical. In only those solvents which give the transient radical, CIDNP nmr emission in the N-methyl region is observed. It is suggested that the emitting species is solvent radical-dimethylamino radical combination product, and that the transient radical is that derived by hydrogen abstraction from this material.

Wieland<sup>1</sup> showed in 1912 that the decomposition of tetraethyl-2-tetrazene (**1b**) with aqueous hydrochloric acid gave nitrogen, acetaldehyde, ethylamine, and diethylamine. He interpreted the reaction as proceeding by heterolytic cleavage of the protonated tetrazene to diethylamino diazonium ion, which decomposed by loss of a proton and nitrogen to give acetaldehyde ethylimine. The discovery that tetramethyl-2-tetrazene (**1a**) gives tetramethylhydrazine (**2**) radical cation upon treatment with acetic anhydride<sup>2</sup> suggested that homolytic cleavage of acylated tetrazene (cation) was possible. Methylation of **1a** also gave **2**,<sup>3</sup> presumably by a similar route.



### Results and Discussion

As previously reported,<sup>2</sup> treatment of **1a** with acetic, trifluoroacetic, benzoic, maleic, succinic, phthalic, or dichloromaleic<sup>4</sup> anhydrides in DMF or acetonitrile results

(1) H. Wieland, *Ann.*, **392**, 133 (1912).  
(2) S. F. Nelsen, *J. Am. Chem. Soc.*, **88**, 5666 (1966).  
(3) W. H. Bruning, C. J. Michejda, and D. Romans, *Chem. Commun.*, 11 (1967).

in nitrogen evolution and the formation of **2**<sup>·+</sup>. When a study of the rate of nitrogen evolution from the reaction with acetic anhydride was attempted, it became obvious that a complicated reaction was taking place. In cumene at 50°, the rate of nitrogen evolution increased almost as rapidly as the square of initial anhydride concentration (at 0.19 M **1a**, 1.57 M Ac<sub>2</sub>O gave a rate constant of 2.5 × 10<sup>-4</sup> sec<sup>-1</sup>; 2.25 M, 4.9 × 10<sup>-4</sup>; 3.26 M, 9.4 × 10<sup>-4</sup>); only 69–74% of the theoretical N<sub>2</sub> was evolved, and there was an induction period corresponding to about one half-life of the final rate constant observed. The reaction was strongly catalyzed by added acetic acid (1 M in Ac<sub>2</sub>O, 1 M in HOAc gave a rate of about 6 × 10<sup>-3</sup> sec<sup>-1</sup>) and the nitrogen yield increased to over 95% of theoretical. Studies were also carried out at 30° in carbon tetrachloride, this solvent giving substantially greater rates than cumene. With just acetic acid, long induction periods were observed. The length of the induction period was shorter and final rate observed larger if nitrogen was not bubbled through the solution before introduction of **1a** to start the reaction; neither was very reproducible, probably due to difficulties in complete removal of oxygen.

Titration of **1a** with hydrochloric acid in water showed that pK<sub>a</sub> of (H-**1a**)<sup>+</sup> is about 3.9 ± 0.1; **1a** did not become detectably diprotonated even in 0.5 M hydrochloric acid. Thus a significant fraction of **1a** should become protonated upon mixing with acetic

(4) High concentrations give a different radical.<sup>2</sup>