Photoaddition and Photoreduction Reactions of Azastilbenes. Solvent Effects on the Photoreactivity of Aza Aromatics[1,2]

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Abstract: An investigation of the direct and sensitized photoreactions of several azastilbenes (stilbazoles and 1,2-bispyridylethylenes) is reported. Direct irradiation of trans isomers of the azastilbenes leads to fluorescence, trans–cis isomerization, and photoreduction and photoaddition reactions. Although fluorescence is nearly solvent independent, isomerization and reduction are strongly medium sensitive. Reduction (and addition) occurs only in the presence of hydrogen atom donating solvents. The direct isomerization efficiency of several isomers increases with increase in solvent polarity. Photosensitization in all solvents investigated results only in cis–trans isomerization. Differential quenching results for direct and sensitized isomerization indicate that the triplet state is not formed efficiently on direct irradiation of most azastilbenes. Photoreduction and photoaddition evidently arise from a low-lying ^{1}n,π^* state, isomerization from a twisted $^1\pi,\pi^*$ state, and fluorescence from the initially formed trans-planar $^1\pi,\pi^*$ state.

The photochemical reactions and spectroscopy of free base nitrogen heteroaromatic compounds have been the subject of considerable investigation and some controversy. For many of the larger aza aromatics similarities of absorption and fluorescence spectra to those of the corresponding hydrocarbons as well as other evidence indicate that hydrocarbon-like $^1\pi,\pi^*$ states with reasonable lifetimes are important intermediates for the nitrogen compounds. Many aza aromatics do, in fact, undergo the same photoreactions as the parent hydrocarbons. However, several of the nitrogen compounds simultaneously exhibit photoreactions from excited singlet states quite unlike those of their hydrocarbon counterparts. A variety of reactions including photochemical addition, reduction, substitution, and elimination processes have been observed which evidently originate *via* hydrogen atom abstraction by an electron-deficient nitrogen.[4–7]

Our investigations of the photoreactions of free-base *N*-heteroaromatics have concentrated on three "prototype" systems; acridine, the azastilbenes, and azaphenanthrenes. In studies with acridine[8] we investigated the effect of various hydrogen atom donors on photoreduction and fluorescence. Both of these processes occur from excited singlet states of acridine.[9–11] However, through a kinetic study of these processes we were able to show that the fluorescent (π,π^*) state is not the reactive species in photoreduction; although photoreduction efficiences show the expected linear Stern–Volmer relationship ($1/\phi_{\mathrm{red}}$ *vs.* 1/[DH], where DH = hydrogen donor and ϕ_{red} is the photoreduction quantum efficiency), acridine fluorescence is not quenched by several hydrogen donors. Even in the single case where fluorescence quenching occurs (DH = *p*-methylanisole), the minimal quenching is inconsistent with the involvement of a single excited singlet state in both processes. Evidently for acridine the state reactive in photoreduction is a low lying ^{1}n,π^* state. The evidence indicates that the ^{1}n,π^* state lies lower in energy than the fluorescent $^1\pi,\pi^*$ state and is spectroscopically hidden; population of the ^{1}n,π^* state of acridine is reversible in certain cases but equilibrium is not attained.[8] The lifetime of the ^{1}n,π^* state of acridine is estimated to be *ca.* 5×10^{-9} sec.

In the present paper we report results of an investigation of the various azastilbenes (stilbazoles and 1,2-bispyridylethylenes) in several solvents. Previous to the present study the photochemistry of these compounds was characterized by three processes: cis–trans isomerization, cyclization to azaphenanthrenes, and fluorescence.[12–14] In a preliminary communication we reported photoaddition and photoreduction reactions of 1,2-bis(4-pyridyl)ethylene (4,4′-BPE) which occur in both hydrocarbons and in 2-propanol. Careful investigation revealed that these photoproducts were formed *via* excited singlet states. However, as was observed with acridine, the fluorescent singlet was found not to be the reactive state; a kinetic study revealed a lower-lying singlet state, evidently a spectroscopically hidden ^{1}n,π^* state, is the reactive intermediate.

Results of the present study of the simultaneous reactivity of π,π^* and n,π^* states in the isomeric azastilbenes suggest that low-lying spectroscopically hidden ^{1}n,π^* states are probably a general phenomenon for aza aromatics. An investigation of the solvent effects on the various photoprocesses has proved particularly use-

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(1) A preliminary account of a portion of this work has appeared: D. G. Whitten and Y. J. Lee, *J. Amer. Chem. Soc.*, **92**, 415 (1970).

(2) Abstracted from the Ph.D. Thesis of Y. J. Lee, University of North Carolina, Chapel Hill, N. C., 1971.

(3) Alfred P. Sloan Foundation Fellow.

(4) For a review see P. Beak and W. R. Messer in "Organic Photochemistry," Vol. II, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, p 117.

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ful in elucidating the role and lifetimes of the "hidden" n,π^* states.

Experimental Section

Materials. Preparation and purification of trans isomers of the various azastilbenes has been previously described.[14] Cis isomers were obtained by preparative scale biacetyl photosensitized isomerization of trans isomers followed by column chromatography and fractional distillation.[15] Purity of the isomeric azastilbenes was checked by glpc to be greater than 99.7% for all trans isomers. Benzophenone (James Hinton, zone refined) was used as received. Michler's ketone (4,4′-bis(dimethylamino)benzophenone) (K & K) was recrystallized from ethanol, decolorized with carbon, chromatographed over alumina, and recrystallized several times from ethanol until colorless crystals were obtained. Triphenylene (Aldrich) was recrystallized twice from 95% ethanol and its purity determined by glpc to be greater than 99.5%. Azulene (Aldrich) was twice vacuum sublimed before use. Benzene (James Hinton, 99.99%, zone refined), and methylcyclohexane and 2-propanol (both Matheson Coleman and Bell, Chromatoquality) were used as received. *tert*-Butyl alcohol (Eastman) was purified by crystallization, followed by treatment with metallic sodium and distillation. Acetonitrile (Eastman spectral quality) was distilled from phosphorus pentoxide.

Spectra. Ultraviolet absorption spectra were recorded on either a Cary 14 or a Unicam SP 800 B spectrophotometer. Fluorescence spectra were recorded using a Hitachi Perkin-Elmer MPF-2A fluorescence spectrophotometer. Fluorescence quantum yields for the azastilbenes were determined using *trans*-stilbene ($\phi_f = 0.05$)[16] at 25° as a reference. (Relative peak areas determined by cutting and weighing.) Either true-bore cylindrical tubes or 1-cm square cells were used. Solution concentrations were adjusted to the same optical density ($\sim$0.5) at the excitation wavelength (300 nm). Samples were deoxygenated either by bubbling with argon or by the freeze-pump-thaw technique; in most cases fluorescent lifetimes were so short that degassing made no significant difference. Fluorescence yields in different solvents were corrected for differences in solvent refractive index.[17] Samples for investigation of temperature effects were degassed by the freeze-pump-thaw method and sealed.

Irradiation Procedures. Quantum yields for the photoaddition and photoisomerization reactions were obtained by irradiating 3-4 ml samples in Pyrex ampoules degassed by three cycles of freeze-pump-thaw. The ampoules were irradiated in a merry-go-round apparatus with light from a medium-pressure mercury lamp. Ferric oxalate actinometry was used to measure light intensities. To isolate the mercury emission lines at 313 and 366 nm, the following filters were used: 313 nm, 7-54 Corning glass filter and a 0.7-cm path, 0.0025 *M* K_2CrO_4 in 1% Na_2CO_3; 366 nm, Corning filters 0-52 and 7-37. Samples were analyzed by glpc on either a Perkin-Elmer 881 or Hewlett-Packard 5754 chromatograph using the following columns: 8 ft × $^1/_8$ in. column of 5% SE30 on Chromosorb G, 8 ft × $^1/_8$ in. column of 10% SE30 on Chromosorb G, 6 ft × $^1/_8$ in. of W98 on Chromosorb G and 8 ft × $^1/_8$ in. of 8% Dow-Corning fluorosilicate on Diatoport S. Internal standards were added after the irradiation. Reactions were carried out to less than 10% conversion; dilute samples were concentrated under reduced pressure prior to analysis. Individual quantum yield determinations were carried out in triplicate; most of the listed data are results of several individual determinations. For studies of the temperature effects, the water bath surrounding the merry go round was heated *via* a silicone heating rod (400-W) controlled by a Variac.

Photoaddition and Photoreduction of Bispyridylethylenes in 2-Propanol. The following is typical of the procedures used in isolation of the products from the photoaddition reactions in hydrocarbon or alcohol solution. *trans*-4,4′-BPE (1.5 g) was dissolved in 1.3 l. of purified 2-propanol. The solution was purged with oxygen-free nitrogen and irradiated with a medium-pressure mercury lamp filtered with a Pyrex sleeve. The progress of the reaction was followed by analytical glpc of aliquots; the reaction was continued a total of 18 hr until only the three major products were present (only small traces of *cis*- and *trans*-4,4′-BPE remained at this point) in a ratio of approximately 5:1:3, listed in order of increasing glpc retention times. The products were separated *via* column chromatography over alumina. (Preparative glpc was also used in several cases.) The first compound collected (eluting with 10% methylene chloride in hexane) was the major component which proved to be the reduction product of 4,4′-BPE, 1,2-bis-(4-pyridyl)ethane (**2**). The white crystalline product, mp 110,° had uv and nmr spectra identical with those of an authentic sample (Aldrich). *Anal.* Calcd for $C_{12}H_{12}N_2$: C, 78.30; H, 6.50; N, 15.20. Found: C, 78.29; H, 6.62; N, 15.01. The second major fraction eluted from the alumina was an oil which consisted of approximately 90% of the third component listed above. Mass spectral analysis revealed major peaks at *m/e* 242 (4,4′-BPE + 2-propanol), 227, 209, and 184. The uv spectrum of this product was similar to those of 4-picoline and the reduction product, 1,2-bis-(4-pyridyl)ethane. It was thus identified as the isopropyl alcohol adduct of 1,2-bis(4-pyridyl)ethylene (**3a**). The minor component of the reaction was identified as 3,6-diazaphenanthrene formed by comparison of its uv spectrum and glpc retention times with those of an authentic sample.[18]

Results

Sensitized Reactions of the Azastilbenes. In previous studies[14,19] it was found that the stilbazoles and bispyridylethylenes undergo reasonably efficient cis-trans isomerization in benzene solutions with high energy sensitizers such as benzophenone and triphenylene. In benzene solution even long-term photosensitization experiments produce isomerization as the only reaction. Studies in benzene with benzophenone as photosensitizer and azulene as a quencher indicated that for several azastilbenes, activation of either cis or trans resulted in totally efficient formation of a common triplet (or equilibrating triplets) which was the isomerization precursor.[14] In the present study it was found that cis-trans isomerization is the only detectable reaction of the several azastilbenes in a variety of solvents. As data in Table I indicate, the quantum efficiency, $\phi_{t\to c}$, for benzophenone sensitized isomerization is relatively little affected by changing the solvent from benzene to *tert*-butyl alcohol or aqueous acetonitrile.

Table I. Quantum Yields for the Benzophenone Sensitized Isomerization of Azastilbenes in Various Solvents[a]

Compound	Benzene	*tert*-Butyl alcohol	Acetonitrile-water[b]
	$\phi_{t\to c}$		
2-Stilbazole	0.44	0.40	0.42
3-Stilbazole	0.44	0.33	0.39
4-Stilbazole	0.40	0.28	0.33
2,2′-BPE	0.50	0.51	0.51
3,3′-BPE	0.51	0.47	0.37
4,4′-BPE	0.44	0.42	0.44

[a] Azastilbene concentration, 0.005 *M;* benzophenone, 0.05 *M;* temperature 25°. Correction for back reaction is made. [b] 70:30 by volume.

Irradiation of solutions of *trans*-1,2-bis(4-pyridyl)ethylene (4,4′-BPE) in 2-propanol with triphenylene or Michler's ketone as the light-absorbing sensitizer led also to cis-trans isomerization with high efficiency as the only detectable reaction. Even solutions exposed to a total dose in excess of 3×10^3 photons/molecule of *trans*-4,4′-BPE yielded the cis isomer as the only product.

The effect of azulene on the cis-trans isomerization quantum yields and stationary state ratios can be used to provide a measure of the olefin triplet lifetime for stil-

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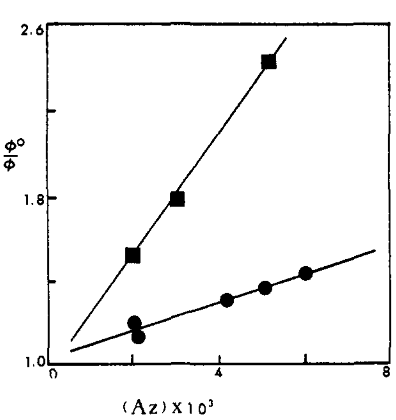


Figure 1. Effect of azulene on the quantum yields for the direct (●) and sensitized (■) isomerization of *trans*-4,4′-BPE.

bene[20,21] and the azastilbenes.[14] The simplest mechanism consistent with the effect of azulene (or other low energy triplet acceptor) on the isomerization of olefins such as a stilbene is outlined in eq 1–6

$$S_0 \longrightarrow S^{1*} \longrightarrow S^{3*} \tag{1}$$

$$S^{3*} + \textit{trans}\text{-olefin} \longrightarrow t^* + S_0 \tag{2}$$

$$S^{3*} + \textit{cis}\text{-olefin} \longrightarrow t^* + S_0 \tag{3}$$

$$S^{3*} + A_0 \xrightarrow{k_4} A^{3*} + S_0 \tag{4}$$

$$t^* \xrightarrow{k_d} [\alpha](\textit{trans}\text{-olefin}) + [1-\alpha](\textit{cis}\text{-olefin}) \tag{5}$$

$$t^* + A_0 \xrightarrow{k_q} A^{3*} + \textit{trans}\text{-olefin} \tag{6}$$

where S = sensitizer, t* = common olefin triplet or equilbrating triplets, A = azulene, and α and $[1 - \alpha]$ represent the fraction of t* decaying to trans and cis, respectively, in the absence of quenching. Using the usual steady state approximations, eq 7 can be obtained for the trans/cis stationary state

$$(t/c)_s = \frac{k_3}{k_2}\left(\frac{\alpha}{1-\alpha} + \frac{k_q[A_0]}{k_d(1-\alpha)}\right) \tag{7}$$

Addition of azulene reduces isomerization quantum yields by quenching of olefin triplets, by internal filtering, and by quenching of sensitizer triplets. The latter two factors can be compensated for by using *trans*-1,2-diphenylpropene ($\phi_{t\rightarrow c} = 0.55$),[22] whose triplets are not quenched by azulene, as an actinometer. From these quantum yields, ϕ = (rate of isomerization)/(rate of formation of excited olefin), the usual Stern–Volmer relationship (eq 8) can be obtained[23]

$$\phi^0/\phi = 1 + k_q\tau[A] \tag{8}$$

Values of $k_q\tau$ measured by eq 7 and 8 are listed in Table II together with the comparable values for stilbene. Figure 1 compares plots for direct and sensitized reactions of 4,4′-BPE. Since it is reasonable to assume that azulene quenches stilbene triplets and azastilbene triplets at the same rate, these values provide an estimate of the relative lifetimes of the various azastilbenes in *tert*-butyl alcohol and in benzene. It has recently been shown that the stilbene triplet lifetime increases ninefold on changing solvent from benzene to *tert*-butyl alcohol.[20] All of the azastilbenes investigated have slightly longer lifetimes than stilbene in benzene.

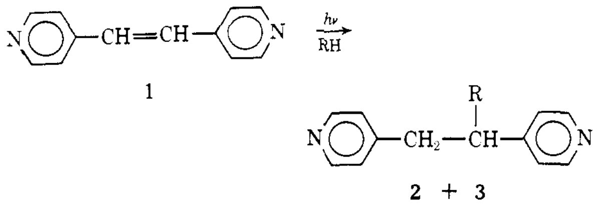
Table II. Azulene Effects on Benzophenone Sensitized Isomerization of Azastilbenes[a]

Compound	Benzene solvent $k_q\tau$,[b] M^{-1}	Benzene solvent Rel lifetime	*tert*-Butyl alcohol solvent $k_q\tau$,[c] M^{-1}	*tert*-Butyl alcohol solvent Rel lifetime
Stilbene[d]	53	1	79	8.8
4-Stilbazole	103	1.9	130	15
3,3′-BPE	104	2.0	250	28
4,4′-BPE	62	1.2	280	31

[a] Olefin concentration, 0.005 *M;* benzophenone, 0.05 *M;* temperature 25°. [b] Value obtained from plot of $(t/c)_{pss}$ *vs.* azulene concentration, see ref 20. [c] Value obtained from Stern–Volmer plot of initial quantum efficiencies. [d] Data from ref 20.

Direct Excitation of Azastilbenes. In contrast to the situation where the azastilbenes are activated by photosensitization, direct irradiation of the azastilbenes can lead to a variety of products *via* paths which are strongly solvent dependent. Three processes have been observed on direct irradiation of trans isomers of the azastilbenes; fluorescence, trans–cis isomerization, and photoreduction–addition reactions. The most precise and extensive data regarding the latter reaction have been obtained for the reactions of *trans*-1,2-bis(4-pyridyl)ethylene.

Photoaddition Reactions of *trans*-1,2-Bis(4-pyridyl)ethylene. As previously reported, direct irradiation of *trans*-4,4′-BPE in benzene results only in very weak fluorescence and extremely inefficient production of the cis isomer as the only primary processes.[14] In contrast, when *trans*-4,4′-BPE was irradiated in hydrocarbon (methylcyclohexane or hexane) or 2-propanol solution, it was found that additional products are formed with low quantum efficiencies.[1] The formation of new products detectable by glpc is accompanied by loss of the ultraviolet absorption of the azastilbene (250–300 nm) and a build-up of a new absorption having λ_{max} 255 nm. The spectra of the isolated products were all nearly identical with the uv spectrum of 4-picoline. These products proved to be substituted 1,2-bis(4-pyridyl)ethanes formed by addition of hydrogen or solvent across the acyclic double bond (eq 9). In a typical experiment irradiation of a solution of **1** and 2-propanol with a medium-pressure mercury lamp (Pyrex filter), until glpc analysis revealed no detectable *cis*- or *trans*-**1** remained, resulted in a 21% yield of **2** and a 28% yield of **3a**. A 2% yield of 3,6-diazaphenanthrene was obtained in addition to *ca.* 2% of an unidentified product so that 53% of the starting material could be



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(9)

2 + **3**

2, R = H
3a, R = $C(CH_3)_2OH$
3b, R = C_7H_{13}

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(20) J. Saltiel and E. D. Megarity, *J. Amer. Chem. Soc.*, **94**, 2742 (1972); 91, 1265 (1969).
(21) J. Saltiel, *ibid.*, **89**, 1036 (1967); 90, 6394 (1968).
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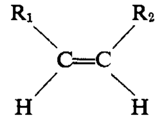
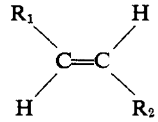
Table III. Initial Quantum Yields for Conversion of 4,4′-BPE to 1,2-Bis(4-Pyridyl)ethane[a]

	Solvent					
	Benzene	Methylcyclohexane	*p*-Methylanisole	2-Propanol	*tert*-Butyl alcohol	Acetonitrile–water[b]
$\phi_{t\to 2}$	0	0.0004	0.0008	0.02	0	0

[a] Degassed solutions, 4,4′-BPE concentration, 0.005 *M*, temp 25°. [b] 70:30 by volume.

Table IV. Products of Long-Term Irradiation of Azastilbenes in 2-Propanol[a]

	Compound						
	2-Stilbazole	3-Stilbazole	4-Stilbazole	2,2′-BPE	2,3′-BPE	3,3′-BPE	4,4′-BPE
	Irradiation time, hr						
	72	72	72	28	42	42	25
Product	% determined						
	54	60	77.0	6	68	81.5	0.2
	5.5	15.5	23	2.5	15.5	16.5	
$R_1CH_2CH_2R_2$[b]	39.5			10.5	2		39
Solvent[b] adduct				80.5	13		52
Phenanthrene[b] derivative	~1	24.5			1	2	4

[a] Degassed solutions irradiated with a medium pressure mercury lamp in a merry-go-round through a Pyrex filter. [b] Determined by glpc; analysis by uv and mass spectra of material collected by preparative glpc.

accounted for.[24] Table III lists quantum efficiencies for formation of **2** in various solvents. Although **2** is not a primary photoproduct of **1** in benzene or *tert*-butyl alcohol, solvents not having readily donatable hydrogens, long-term irradiation of **1** in benzene leads to slow formation of roughly equal quantities of 3,6-diazaphenanthrene and **2** in what amounts to a net disproportionation process.

Photoaddition Reaction of Other Azastilbenes. In addition to **1** several other azastilbenes were found to undergo photoreduction of the acyclic double bond and addition of solvent in 2-propanol. In all cases quantum efficiencies for formation of the reduced product and solvent adducts were relatively low. Table IV summarizes the results of long-term irradiation of several azastilbenes in 2-propanol. Although extensive characterization of all of the products for each azastilbene was not carried out, the reduced product and solvent adducts were readily identified by their characteristic uv and mass spectra. The azaphenanthrenes were likewise easily identifiable by spectral methods.[18] Of the seven azastilbenes investigated, only three, 3- and 4-stilbazole and 3,3′-BPE, did not readily form adducts on direct irradiation. For all compounds, direct irradiation in *tert*-butyl alcohol under similar conditions for the same amount of time resulted only in cis–trans isomerization. Photoreduction was only observed when the azastilbenes were irradiated in a *solvent* containing readily donatable hydrogen atoms. Irradiation of azastilbenes in dilute solutions of hydrogen atom donors such as tri(*n*-butyl)tin hydride or triphenylmethane (0.005 *M*) did not lead to appreciable reduction.

Table V. Quantum Yields for Azastilbene Fluorescence in Various Solvents

	ϕ_f			
Compound	Benzene	2-Propanol	*tert*-Butyl alcohol	Acetonitrile–water[b]
3-Stilbazole	0.07	0.04	0.05	0.05
4-Stilbazole	0.005	0.003	0.003	0.002
3,3′-BPE	0.04	0.10	0.12	0.10
4,4′-BPE	0.0004	0.0004	0.0004	0.0004

[a] Values measured using *trans*-stilbene (ϕ_f = 0.05) as a reference. Corrected for variations in solvent refractive index (ref 17). [b] 70:30 by volume.

Solvent Effects on Azastilbene Fluorescence. All of the *trans*-azastilbenes exhibit fluorescence in benzene having dispersion spectra similar to that of *trans*-stilbene.[14] However, with two exceptions, 3-stilbazole and 3,3′-BPE, the quantum efficiencies of fluorescence are much lower than that of stilbene. The room-temperature fluorescence of four "representative" azastilbenes was investigated in a series of solvents (Table V). For benzene, 2-propanol, and *tert*-butyl alcohol as solvents each of the four azastilbenes exhibited fluoresence showing little change in dispersion or quantum efficiency with change in solvent. When the solvent was changed from one of the former to aqueous acetonitrile there was a pronounced shift in the fluorescence spectrum to longer wavelengths in each case; however, as data in Table V indicate, the quantum efficiency of fluorescence is little changed in aqueous acetonitrile for any of the isomers examined. It has previously been shown that the ground states of most azastilbenes have pK_A ~ 5 such that protonation is not important in neutral aqueous media.[25,26] How-

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[24] In short term low per cent conversion experiments much better mass balances were obtained.

[25] G. Cauzzo, G. Galiazzo, U. Mazzucato, and N. Mongiat, *Tetrahedron*, **22**, 589 (1966).

[26] G. Beggiato, G. Favaro, and U. Mazzucato, *J. Heterocycl. Chem.*, 7, 583 (1970).

ever, the fluorescent singlets of several azastilbenes can be estimated to have $pK_A \sim 10^{12}$[27] such that in aqueous acetonitrile it is likely that the fluorescence observed arises at least in part from protonated excited singlets.

The fluorescence of *trans*-3,3′-BPE and *trans*-4,4′-BPE is rather strongly temperature dependent (Table VI); in each case lowering the temperature in *tert*-butyl alcohol causes an increase in fluorescence efficiency. For *trans*-3,3′-BPE decreasing the temperature of an EPA solution from 298°K (fluid) to 77°K (glass) causes an increase of the fluorescence yield to near unity.[28] For *trans*-4,4′-BPE a similar experiment in EPA produces only a slight increase in fluorescence; even under conditions where rotation is restricted, fluorescence for *trans*-4,4′-BPE remains an extremely inefficient process.

Table VI. Solvent/Temperature Effect on the Fluorescence of *trans*-3,3′-BPE and *trans*-4,4′-BPE

Temp, °K	Solvent	ϕ_f[a] 3,3′-BPE	ϕ_f[a] 4,4′-BPE
298	EPA	0.107	0.0005
77	EPA	1.01 ± 0.15	0.0001 ± 0.001
333	*tert*-Butyl alcohol	0.07	0.0003
313	*tert*-Butyl alcohol	0.08	0.0005
303	*tert*-Butyl alcohol	0.10	0.0007

[a] Quantum yields measured using *trans*-stilbene (ϕ_f = 0.05) as a reference.

Solvent Effects on the Direct Trans–Cis Photoisomerization. It has been previously reported that the direct isomerization quantum yields for the stilbazoles are strongly solvent dependent.[12,30] For 2- and 4-stilbazole it has been found that addition of proton sources in nonaqueous solutions causes a sharp decrease in the trans → cis quantum efficiencies.[12] Under the same conditions the yields for 3-stilbazole are reported to increase significantly. These affects have been attributed, at least in part, to protonation of excited singlet states of 2- and 4-stilbazole.

In the present study it was found that quantum efficiencies for the trans → cis process for the stilbazoles generally decrease in the series: benzene, 2-propanol, *tert*-butyl alcohol (Table VII).[31] For all three compounds the isomerization efficiency dropped sharply on going to acetonitrile–water. In contrast with the stilbazoles, three of the 1,2-bispyridylethylenes investigated showed increases in isomerization efficiencies as solvent polarity increased. A fourth, *trans*-2,3′-BPE, showed very little effect of changing solvent under the conditions employed. The changes observed were modest (fourfold) for *trans*-3,3′-BPE but quite pronounced for *trans*-2,2′-BPE (tenfold) and *trans*-4,4′-BPE (100-fold) (Table VII). The isomerization quantum yields, $\phi_{t\rightarrow c}$, for both *trans*-3,3′-BPE and *trans*-4,4′-BPE increase with temperature in *tert*-butyl alcohol. For *trans*-3,3′-BPE the increase is significant; $\phi_{t\rightarrow c}$ increases from 0.18 at 20° to 0.36 at 50°. The increase for *trans*-4,4′-BPE is slight by comparison; $\phi_{t\rightarrow c}$ is 0.075 at 20° and 0.08 at 50°.

Table VII. Quantum Yields for the Direct Trans–Cis Isomerization of Azastilbenes in Various Solvents[a]

	$\phi_{t\rightarrow c}$[b]			
Compound	Benzene	2-Propanol	*tert*-Butyl alcohol	Acetonitrile–water[c]
2-Stilbazole	0.28	0.34	0.24	0.04
3-Stilbazole	0.35	0.31	0.26	0.13
4-Stilbazole	0.37	0.31	0.22	0.07
2,2′-BPE	0.01	0.017	0.02	0.10
2,3′-BPE	0.23	0.25	0.26	0.22
3,3′-BPE	0.08	0.23	0.24	0.38
4,4′-BPE	0.003	0.04	0.08	0.25

[a] Degassed solutions, azastilbene concentration, 0.005 *M*, temperature = 25°. [b] Precision for all values better than ±10%. [c] 70:30 by volume.

Azulene Quenching of Direct Photoisomerization. Azulene quenching of the direct trans → cis process of most azastilbenes can be conveniently assessed by measuring initial isomerization efficiencies at 313 nm. For 4-stilbazole, 3,3′-BPE, and 4,4′-BPE, data on the azulene effect on direct isomerization in *tert*-butyl alcohol yields good linear Stern–Volmer plots (Figure 1) of the form[32]

$$\phi^0_{t\rightarrow c}/\phi_{t\rightarrow c} = 1 + S[A] \qquad (10)$$

Slopes (S) for these plots were 18, 90, and 70 M^{-1} for 4-stilbazole, 3,3′-BPE, and 4,4′-BPE, respectively. Interestingly the slopes for the plots of the BPE derivatives are much larger than the slope/intercept ratio of 16.1 M^{-1} for the plot of the stilbene trans/cis ratio at the photostationary state *vs.* [azulene].[20]

Discussion

Intersystem Crossing in the Azastilbenes. The only process common to both direct and sensitized activation of the azastilbenes is cis–trans isomerization. Previous studies of the direct and sensitized isomerization in benzene established that maximum efficiencies of intersystem crossing for the 1,2-bispyridylethylenes were very low, since, although triplets isomerize with high efficiency, direct photolysis causes very inefficient cis–trans isomerization.[14,19] For the stilbazoles relatively efficient isomerization was observed in both direct and sensitized experiments such that the occurrence of efficient intersystem crossing could not be excluded.[14,33] Results obtained in the present investigation indicate that for the azastilbenes, contrary to our previous interpretation,[14] intersystem crossing *does not occur* with measurable efficiencies and that the direct and sensitized isomerization pathways probably do not proceed through a common excited state.[23] This conclusion is based on evaluation of the differential quenching of the direct and sensitized isomerization in *tert*-butyl alcohol by azulene. For each of the three

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(27) A. Weller, *Progr. React. Kinet.*, **1**, 189 (1961).

(28) Saltiel and D'Agostino[29] have separated the temperature effect for *trans*-3,3′-BPE in *tert*-butyl alcohol into a viscosity effect and a true temperature effect caused by an inherent thermal barrier of 2.5 kcal/mol for escape from the fluorescent state. This compares with a barrier of 3.5 kcal/mol for the presumed same process in stilbene.[29]

(29) J. Saltiel and J. T. D'Agostino, in preparation for publication. We thank Professor Saltiel for sending us a preprint of this manuscript.

(30) P. Bortulus, G. Cauzzo, U. Mazzucato, and G. Galiazzo, *Z. Phys. Chem. (Frankfurt am Main)*, **63**, 29 (1969).

(31) The decrease from 2-propanol to *tert*-butyl alcohol is probably due to a viscosity increase in the latter solvent.[29]

(32) The quantum yields were obtained using 313 nm light with [azastilbene] = 5×10^{-3} *M*. Quantum yields are corrected for the small amount of internal filtering by azulene.

(33) P. Bortulus, G. Favaro, and U. Mazzucato, *Mol. Photochem.*, **2**, 311 (1970).

azastilbenes on which this study was carried out (4-stilbazole, 3,3′-BPE, and 4,4′-BPE), the effect of azulene on both direct and sensitized trans → cis isomerization initial quantum efficiencies leads to good linear Stern–Volmer plots (Figure 1) which follow eq 10. In each case, the slope of the plot for the direct isomerization is *much smaller* than the slope for the sensitized reaction. Evaluation of the various kinetic possibilities for isomerization indicates that this behavior is consistent only with a singlet path for the direct isomerization *which bypasses the triplet state.*[34–37]

Deactivation of Azastilbene Excited Single States. Further analysis of the azulene quenching experiments in the direct irradiation of the azastilbenes enables some conclusions regarding the paths for deactivation in the excited singlet manifold. The estimated value of $k_f = 4 \times 10^8$ sec^{-1} (±20%) from absorption spectra for all azastilbenes is the same as calculated for *trans*-stilbene.[14,20] However, with the exception of 3-stilbazole and 3,3′-BPE, the fluorescence efficiencies for the azastilbenes are much lower than that for stilbene, indicating that lifetimes for the fluorescent singlets are considerably shorter than the stilbene fluorescent lifetime. For stilbene it has been shown that azulene quenching of the direct isomerization involves long-range excitation transfer from the fluorescent singlet with a viscosity-independent rate constant $k_q^s = 1.2\text{–}1.9 \times 10^{11}\ M^{-1}$ sec^{-1}.[20] The Stern–Volmer treatment for the effect of azulene on the initial quantum efficiencies for isomerization is then given by eq 11 where τ_s is the

$$\phi^0_{t\to c}/\phi_{t\to c} = 1 + k_q^s\tau_s[A] \qquad (11)$$

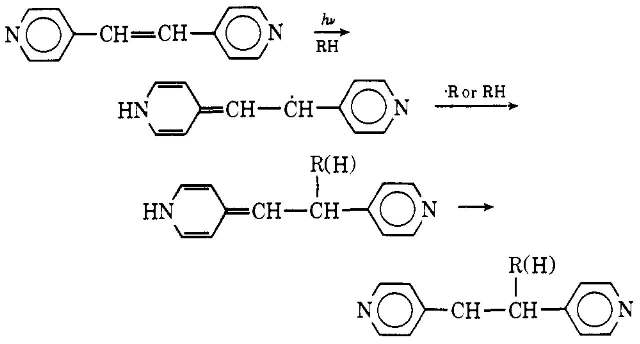
lifetime of the fluorescent singlet. Based on similarities between stilbene fluorescence and fluorescence of the various azastilbenes, it would be reasonable to expect a similar value for k_q^s for transfer to azulene from the various azastilbene fluorescent singlets. Values for an "expected" Stern–Volmer slope, $k_q^s\tau_s$, can be calculated for the azastilbene fluorescent singlets using the k_q^s value for stilbene. Table VIII compares the calculated values with the measured Stern–Volmer slopes for the direct isomerization. For 4-stilbazole and 4,4′-BPE the severe disparity between "calculated" and measured values indicates that the state quenched by azulene in competition with isomerization can not be the fluorescent singlet. This conclusion can also be reached by calculating the fraction of fluorescent singlets quenchable by 0.01 M azulene, concentrations which quench isomerization significantly for all three azastilbenes. For 4-stilbazole the fraction quenched by azulene is calculated to be *ca.* 2% while for 4,4′-BPE the fraction quenched amounts to less than 0.2%.[38] For 3,3′-BPE the slope anticipated for quenching the fluorescent singlet is somewhat smaller than the measured value; it is uncertain, therefore, whether azulene quenching of the direct isomerization of 3,3′-BPE involves exclusively the fluorescent singlet. However it is clear that for 3,3′-BPE, unlike 4-stilbazole and 4,4′-BPE, quenching of the fluorescent singlet by azulene is an important process at moderate azulene concentrations.

Table VIII. Comparison of "Calculated" and Measured Slopes for Azulene Quenching of Azastilbene Direct Isomerization

Compound	"Calculated" $k_q^s\tau_s$, M^{-1}	Measured slope, M^{-1}
4-Stilbazole	1.4	18
3,3′-BPE	66.5	90
4,4′-BPE	0.2	70

Reactivity and Lifetimes of $^1n,\pi^*$ States. Evidently the state intermediate between the fluorescent singlet and the isomerizable species in 4,4′-BPE and several of the other azastilbenes is a planar trans $^1n,\pi^*$ state.[39] It is likely that this is the state responsible for the photoaddition and photoreduction reactions and also the excited singlet state long lived enough to be quenched by azulene. This assignment is based on the evidence that the photoreduction and photoaddition reactions occur only in the presence of hydrogen atom donors, the same hydrogen donors reactive with excited singlets of other N-heteroaromatics such as acridine. In fact the pattern of reactivity for the azastilbenes is quite analogous to that observed previously for acridine.[8] Furthermore the photoreduction and photoaddition reactions do not occur when stilbene or similar diarylethylenes are irradiated in the presence of the same hydrogen atom donors. The likely path for the reaction to form the photoadducts is outlined in Scheme I.

Scheme I



That the reactive $^1n,\pi^*$ states are of lower energy than the fluorescent singlet is indicated by the fact that fluorescence is not quenched or reduced in efficiency in the presence of solvents reactive as hydrogen donors.[40] Some very rough estimates of the lifetime of the $^1n,\pi^*$ states for *trans*-4-stilbazole and *trans*-4,4′-BPE can be made from the azulene quenching data. Since the $^1n,\pi^*$ states are not detectable spectroscopically,[41] they must have very low oscillator strengths. Consequently long-range singlet–singlet energy transfer to azulene by a dipole–dipole interaction is probably unimportant. However azulene should quench the $^1n,\pi^*$

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(34) Several references are available which amplify the various possibilities and anticipated results; in this case the very large differences in the slopes indicate it unlikely that significant triplet state participation can be occurring.

(35) J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2**, 133 (1970).

(36) P. J. Wagner, *ibid.*, **3**, 23 (1971).

(37) T. R. Evans, *Tech. Org. Chem.*, **14**, 336 (1971).

(38) Calculated and "measured" R_0 values for long-range energy transfer are also not in agreement if it is assumed azulene is quenching the fluorescent singlet.

(39) Presumably the twisted singlet state, $^1p^*$, is too short lived to be quenched.

(40) The evidence is perhaps not as conclusive for the azastilbenes as for acridine, since the quantum efficiencies for fluorescence and reduction are so low; however it is clear that if the fluorescent singlet were the reactive state in photoreduction some quenching of fluorescence by reactive hydrogen atom donors should occur.

(41) For some recent spectroscopic studies of n,π* transitions in *N*-heterocyclics see R. D. McAlpine, *J. Mol. Spectrosc.*, **38**, 441 (1971).

states efficiently by a collisional process. If it is assumed that the Stern–Volmer slopes for 4-stilbazole and 4,4′-BPE represent the product of $k_{\text{diff}} = 1.7 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ (for *tert*-butyl alcohol) and τ_n, the lifetime of the $^1n,\pi^*$ state, lifetimes of 10^{-8} sec and 4×10^{-8} sec are obtained for 4-stilbazole and 4,4′-BPE, respectively. The overall path for deactivation probably involves three excited singlet states of the azastilbenes: the initially formed planar trans fluorescent state ($^1\pi,\pi^*$), the $^1n,\pi^*$ state, and a twisted state ($^1\pi,\pi^*$) that decays with isomerization. The trend of increased quantum efficiencies for isomerization with increasing solvent polarity for 2,2′-BPE and 4,4′-BPE can be explained by an increase in energy of the $^1n,\pi^*$ state. Such an increase would be expected to lower the activation energy to reach the twisted state.

The lifetimes and reactivity of $^3n,\pi^*$ states in aza aromatics remain an area for further investigation. Results of the present study suggest that participation of reactive $^3n,\pi^*$ states in sensitized reactions of the azastilbenes is doubtful.

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Polar Exchange of Methylbenzhydryl Iodides with Iodine in Hexane

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Abstract: *m*- and *p*-methylbenzhydryl iodides exchange with elementary iodine in hexane by a polar mechanism requiring two molecules of I_2 in the transition state. Irreproducible parallel contributions by terms of lower order in iodine could be virtually eliminated by coating the glass surface of the reaction vessel with a hydrophobic silicone preparation. These and previous observations at 0° obey the σ^+ modification of the Hammett equation with $\rho = -5.2$; this very large magnitude of substituent effects means that the *p*-methyl compound exchanges 5000 times as rapidly as the *m*-chloro one! It is suggested that the second molecule of iodine interacts with the back side of the incipient carbonium ion in a transition state resembling an $I_2 \cdot \cdot R^+ I_3^-$ ion pair. Attempts to synthesize nitro- and cyanobenzhydryl iodides were frustrated apparently because these compounds are very sensitive to decomposition by radical mechanisms; such decomposition is to be expected for any organic iodide unless the C–I bond is appreciably stronger than the I–I bond in the element.

The effects of meta and para substituents on rates tend to be greatest for those reactions having considerable release of or demand for electrons at the reaction center. Such reactions tend to have polar transition states, and especially large substituent effects should be observed in solvents of low dielectric constant where compensatory polarization of the medium is less important. Some organic iodides undergo isotopic exchange with the element by a very polar mechanism in which the transition state approximates an ion pair,[1] and Muizebelt and Noyes[2] have shown that benzhydryl iodide and its monochloro derivatives exchange by such a mechanism even in hexane solvent. The present work was undertaken to study additional substituents and to determine the magnitudes of their effects on this very polar reaction in a solvent of very low dielectric constant.

Experimental Section

Methylbenzhydryl Iodides. A solution of 2 g of *m*- or *p*-methylbenzhydryl alcohol, $(CH_3C_6H_4)(C_6H_5)CHOH$, in 5 ml of ethanol was flushed with nitrogen and treated with 5 ml of a concentrated solution of HI in ethanol and 10 ml of 57% aqueous HI. After 3 min, 20 ml of hexane was added to extract the iodide and was separated from the alcohol 2 min later. This hexane extract was washed with dilute aqueous sodium sulfite and sodium bicarbonate and then with water, dried over magnesium perchlorate for 1 hr, and concentrated by a stream of dry nitrogen. The product was crystallized by cooling the hexane solution to −80°. Four crystallizations normally produced material containing at least 99% of the theoretical amount of iodine.

Because the benzhydryl iodides were rapidly decomposed by light or oxygen, the entire preparation was carried out under a dim red light. The hexane solution was stored at −80° in complete darkness. Samples were analyzed for iodine by dissolving a known weight in carbon tetrachloride, irradiating the solution with a tungsten lamp until the iodine concentration reached a steady value, and measuring that concentration spectrophotometrically. The quantitative validity of this method was checked by hydrolyzing a sample and titrating the liberated iodide potentiometrically with silver nitrate.

Other Benzhydryl Iodides. Attempts were also made to prepare benzhydryl iodides with electron-withdrawing nitro[2] or cyano substituents. The attempts were unsuccessful, apparently because these compounds decomposed by radical mechanisms almost as rapidly as they were formed.

Hexane. The hexane solvent was stirred with concentrated sulfuric acid and then twice with 30% fuming acid, washed with sodium carbonate and water, and dried over calcium chloride. The middle fraction boiled 67.9–68.8° at 750 mm.

Procedure. Stock solutions of labeled iodine were prepared by adding a few drops of aqueous carrier-free iodine-131 to a solution of iodine in hexane and were dried over magnesium perchlorate. Concentrations of iodine were determined spectrophotometrically, and those of organic iodide were determined in the same way after quantitative photolysis.

Kinetic procedures were difficult because the organic iodide was decomposed by light and by oxygen and because the rate of exchange was sensitive to traces of moisture. All operations were conducted

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[1] R. M. Noyes and E. Körös, *Accounts Chem. Res.*, **4**, 233 (1971).

[2] W. J. Muizebelt and R. M. Noyes, *J. Amer. Chem. Soc.*, **92**, 6012 (1970).