

EXCITED STATE REACTIVITY OF AZA-AROMATICS: VI. PHOTOISOMERIZATION OF AZASTILBENES INDUCED BY INORGANIC ANIONS

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Summary

The effect of alkali halides on the fluorescence and photoisomerization of 3-styrylpyridine, its 4'-methoxy derivative and 1,2-di(3-pyridyl)-ethylene, all in their protonated form, has been studied. With the bromide and iodide anions the photoreaction is less quenched than luminescence for 3-styrylpyridine and is even drastically enhanced for the other two compounds. This is explained by the formation of a complex (probably of charge transfer nature) between the protonated azastilbenes and the halide anions followed by the induction of olefin intersystem crossing by heavy atom effect. The kinetic treatment of the proposed reaction scheme allowed the yields of induced intersystem crossing and photoreaction to be obtained.

Introduction

The induction of singlet-triplet intersystem crossing (ISC) by external heavy atoms in some stilbene-like olefins, using *cis-trans* isomerization as a probe, has been recently investigated [1, 2].

In a previous paper [2] we demonstrated that inorganic anions quench the first excited singlet state of azastilbenes (ASs) through a mechanism where probably both the electron donating ability and the heaviness of the quencher come into play. The dependence of the quenching constant K_Q on the oxidation potential of the anion has been taken as an indication of an associative charge transfer (CT) mechanism, even if the absence of complex emission and of radical absorption left open the question about the nature of the intermediate complex [2, 3]. In the experiments with halides as quenchers it has been found that, while fluorescence and photoisomerization

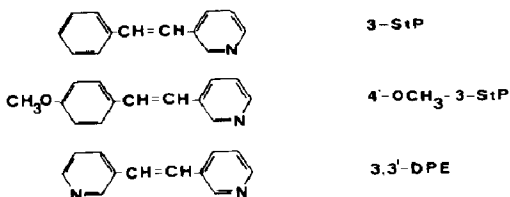
of 3-styrylpyridinium (3-StPH⁺) cations are quenched to the same extent by Cl⁻, the heavier anions Br⁻ and I⁻ strongly quench the fluorescence while the photoreaction is quenched only to a lesser extent, or not at all. This is probably due to an induced ISC to the triplet level where isomerization is known to occur with good yield (~0.5) from sensitized experiments in the presence of triplet donors [4].

It was interesting to investigate the induced ISC of ASs for some compounds characterized by very low photoreaction yield in the absence of quenchers because of fast internal conversion processes. Two available examples are the protonated methoxy derivative of 3-StP (4'-OCH₃-3-StPH⁺) and the diprotonated form of 1,2-di(3-pyridyl)-ethylene (3,3'-DPEH₂²⁺).

This paper reports the results obtained from the study of the fluorescence and photoisomerization quenching of these compounds by halides as well as the information obtained by their kinetic analysis. The ISC induction by halides for the two new compounds investigated proved to be a very efficient way of reducing radiationless decay and bringing about a noticeable increase in the photoreaction yield.

Experimental

The compounds investigated, all in the *trans* form,



were synthesized by standard methods for previous work.

Sodium halides were of analytical grade from Merck.

The fluorescence measurements were performed on a Perkin-Elmer MPF-3 spectrophotofluorimeter with an accessory for spectrum correction using rhodamine B as quantum counter. The emission yields (Φ_{FM}) were measured in dilute solutions (absorbance 0.05 at the analytical wavelength) using 2-(1-naphthyl)-5-phenyl-1,3,4-oxadiazole (α -NPD) as standard. The solutions were de-aerated by bubbling nitrogen. The quenching constants $K_Q(M^{-1})$ were obtained from the Stern-Volmer (SV) equation, where the ratio of the fluorescence quantum yields was approximated to the intensity ratio at the analytical wavelength.

The photoisomerization quenching was studied spectrophotometrically using a Unicam SP500/2 spectrophotometer. The *trans* \rightarrow *cis* quantum yields (Φ_C) were measured at various halide concentrations (up to 1 M) using potassium ferrioxalate as actinometer. The measurements were made on the protonated species in water-ethanol 90/10 (v/v) at pH 2 (Britton buffers)

for the StPs ($pK_a \sim 5$) [5] and at pH 0 (HClO_4) for the DPE ($pK_a^I \sim 5$, $pK_a^{II} \sim 2.5$) [6]. At the latter pH, the quenching measurements in the presence of iodide were not feasible and for this reason the results of Table 1 and Fig. 1 for 3,3-DPEH₂²⁺ are limited to the experiments with Br⁻. The ionic strength was kept constant at $\mu = 1$ and $\mu = 2$ by NaClO_4 for the StPs and the DPE, respectively.

Results and Discussion

Figure 1 shows the SV plots for the fluorescence and photoisomerization yields of three ASs using Br⁻ and I⁻ as quenchers in de-aerated water-ethanol solutions at acidic pH. The protonated cations proved to be more

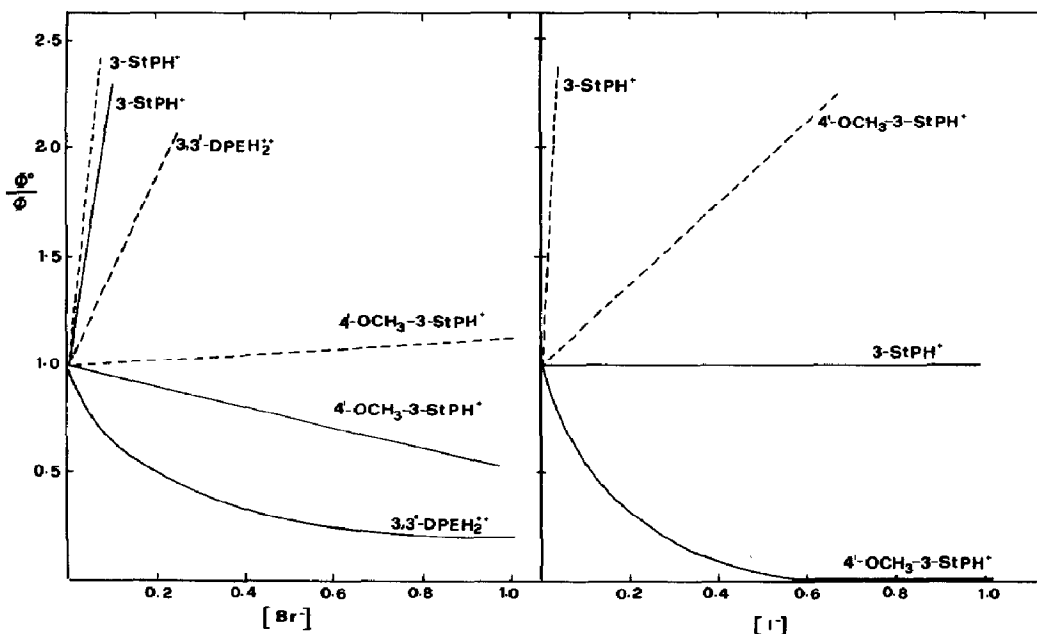


Fig. 1. SV plots for fluorescence (-----) and *trans* \rightarrow *cis* photoisomerization (—) of 3-StPH⁺ and its 4'-OCH₃ derivative (pH = 2, $\mu = 1$) and of 3,3'-DPEH₂²⁺ (pH = 0, $\mu = 2$) by bromide and iodide anions in 90/10 (v/v) water-ethanol.

suitable for such a study since K_Q is higher when the excited species is long living and both partners are charged.

In no case do the fluorescence and photoreaction trends of Fig. 1 coincide. In particular, for the two new compounds investigated the photoreaction plots are not linear and have a negative slope from the beginning showing that the presence of halides induces a very marked increase of the reaction yield. This indicates that the complex E formed by the $\text{ASH}^{*+} + \text{X}^-$ interaction undergoes ISC to the reactive triplet state.

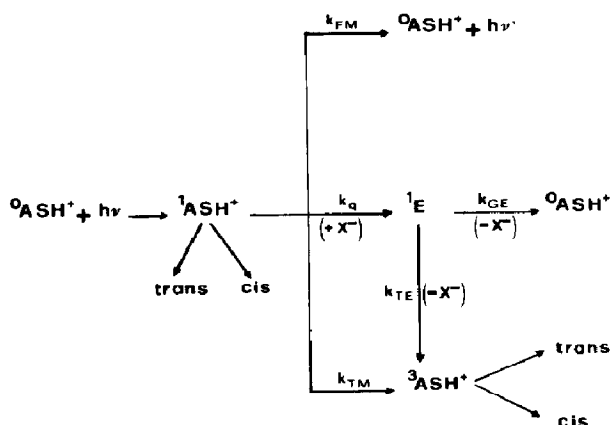
TABLE 1

Quantum yields and quenching parameters from SV plots of fluorescence and photoisomerization of three *trans* azastilbene cations in the presence of halides in water-ethanol 90/10 (v/v).

Compounds	None		Br ⁻		I ⁻			
	Φ_{FM}	Φ_{CM}	K_Q	<i>i/s</i>	Φ_{CE}^{lim}	K_Q	<i>i/s</i>	Φ_{CE}^{lim}
3-StPH ⁺	0.205	0.27	18.8	18.1	0.045	39.0	38.2	0.25
4'-OCH ₃ -3-StPH ⁺	0.012	0.0006	0.14	0.13	0.043	2.0	1.65	0.36
3,3'-DPEH ₂ ²⁺	0.033	0.045	4.3	0.7	0.5			

On the other hand, experiments with Cl⁻ as quencher showed that this anion has the same quenching effect on emission and photoreaction of 3-StPH⁺ and 3,3'-DPEH₂²⁺ while it does not quench at a measurable extent the shorter living methoxy compound. These results indicate that the decay of the complex with Cl⁻ by-passes the triplet manifold, otherwise the quenching of photoreaction would be smaller. Moreover, they show that the complex itself does not isomerize, indirectly indicating that with the heavier quenchers the interaction effect is to open a way for isomerization in the triplet manifold through an enhanced ISC by heavy donors.

The non-linearity of the isomerization plots can be explained by kinetic analysis of the following reaction scheme applied to the *trans* isomer (both the singlet and triplet states of the olefin are considered to be reactive):



where the superscripts have the usual significance and the subscripts XM and XE refer to the processes of fluorescence ($X = F$), internal conversion to the ground state ($X = G$), ISC to the triplet state ($X = T$) and photoisomerization to the *cis* form ($X = C$) for the uncomplexed (M) and complexed (E) excited species. The step represented by k_{TE} does not distinguish between direct

production of the olefin triplet, as shown in the scheme, or through an intermediate 3E which then decomposes to $^3ASH^+$ and X^- .

When all processes are quenched proportionately, the quenching ratio can be related to the quencher concentration by the well known SV-type equation:

$$\Phi_{XM}^{\circ}/\Phi_{XM} = 1 + K_Q [Q] \quad (1)$$

where Φ° is for $[Q] = 0$ and Φ for the concentration $[Q]$. This is the case of the quenching by Cl^- . On the other hand, when fluorescence and photoreaction are quenched to a different extent and one uses the experimentally observed values for the isomerization yield, Φ_C , only the slope of the fluorescence SV plot gives directly the quenching constant $K_Q = k_q \tau_{FM}$. With regard to the photoreaction, however, when the measured yield is greater than expected if fluorescence and photoreaction were quenched proportionately ($\Phi_C > \Phi_{CM}$), the slope of the plot assumes a different meaning. At any $[Q]$, the overall photoreaction yield, Φ_C , is in fact the sum of two contributions, by the excited molecules which are not quenched and react in the uncomplexed form (Φ_{CM}) and those which react through the complex (Φ_{CE}).

The comparison of the emission and photoreaction quenching ratios allows the yield of induced reaction (*i.e.* the fraction of excited molecules which are induced to react through the complex) to be calculated at the various $[Q]$:

$$\Phi_{CE} = \Phi_C - \Phi_{CM} = \Phi_C - \frac{\Phi_{FM}}{\Phi_{FM}^{\circ}} \Phi_{CM}^{\circ} = \frac{k_{CE} \tau_E K_Q [Q]}{1 + K_Q [Q]} \quad (2)$$

where τ_E is the complex lifetime. The last equality, which derives from the application of the photostationary state kinetics to the reaction scheme above, is valid if T_1 is not quenched by the halides [7]. For 4'-OCH₃-3-StPH⁺ this was tested to be true using tris (2,2'-bipyridine) ruthenium (II) as sensitizer. The same sensitized yield was obtained in the presence of 1 M HBr and in absence of perturbers. Equation (2) allows the relation between the *observed* quenching ratio of photoreaction and $[Q]$ to be established:

$$\frac{\Phi_{CM}^{\circ}}{\Phi_C} = \frac{1 + K_Q [Q]}{1 + \frac{\Phi_{CE}^{lm}}{\Phi_{CM}^{\circ}} K_Q [Q]} \quad (3)$$

where the product $k_{CE} \tau_E$ has been substituted by Φ_{CE}^{lm} , which is the induced yield at $[Q] \rightarrow \infty$, when all the excited molecules are in the E form. This equation explains the difference with respect to fluorescence and the non-linearity of SV plots for photoreaction. The limiting induced yield can be calculated from eqn. (3) or from the intercept of the plot $1/\Phi_{CE}$ vs. $1/[Q]$. If the reaction scheme is correct, this plot should be linear and the intercept/slope ratio should be equal to the slope of the SV plot for fluorescence quenching. Figure 2 shows the results obtained for 3-StPH⁺ with the two quenchers. It is worthwhile noting that a similar treatment for the 4'-Br and 4'-I substituted 3-StPH⁺ (which have a higher inherent Φ_{TM} yield) gave no

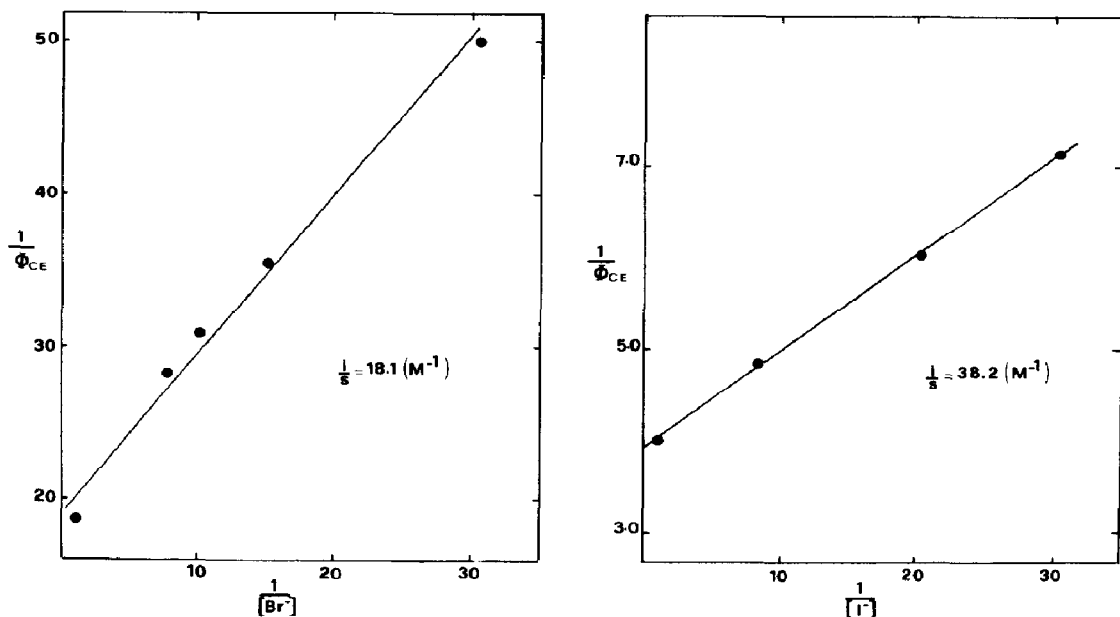


Fig. 2. SV-type plot for *trans* → *cis* photoisomerization of 3-StPH⁺ induced by heavy halide anions in 90/10 (v/v) water-ethanol at pH = 2 and $\mu = 1$.

linear trend. This is probably indicative of an induced $T_1 \rightarrow S_0$ ISC by the inorganic anions in these molecules.

Table 1 shows the quantum yields of fluorescence and *trans* → *cis* photoisomerization in the absence of quenchers, the fluorescence and isomerization quenching constants in the presence of Br⁻ and I⁻ and the maximum yields of induced isomerization for the three ASs in the protonated form. The K_Q values obtained from the fluorescence and photoreaction plots were in good agreement, except in the case of 3,3'-DPEH₂²⁺ where the discrepancy between the two values is certainly greater than the experimental uncertainty for reasons not yet clear. Extrapolation of the plots of Fig. 2 at infinite quencher concentration leads to Φ_{CE}^{lim} values which are particularly high in the case of the compounds with high efficiency of radiationless decay and low inherent isomerization yield.

As expected, the inducing effect depends strongly on the nature of the excited partner. The long living 3-StPH⁺ ($\tau_{FM} = 5.5$ ns) [5], which displays the higher quenching constants, has the lowest inducing effect, while the short living methoxy derivative has small K_Q values and high Φ_{CE}^{lim} values (70 and 600 times higher than the inherent yield, with Br⁻ and I⁻, respectively).

The effect of the anion nature is also expected, the interaction with I⁻ leading to Φ_{CE}^{lim} values 5 - 8 times higher than with Br⁻.

Considering that the sensitized photostationary state measurements in the presence of high energy triplet donors resulted in about 60% of *cis* isomer for many ASs [4,8], one can estimate that the quenching by halides for

the compounds investigated leads to the formation of the reactive triplet with an efficiency going from 7% in the complexes of 3-StPH⁺ and 4'-OCH₃-3-StPH⁺ with Br⁻ to 80% in the case of the complex 3,3'-DPEH₂²⁺ + Br⁻.

It is interesting to note that, changing the nature of the two partners, one passes from the case of the complexes with Cl⁻, where $\Phi_{GE} \sim 1$, $\Phi_{TE} \sim 0$, to the case of 3,3'-DPEH₂²⁺ + Br⁻, where $\Phi_{GE} \sim 0$ and $\Phi_{TE} \sim 1$.

In the case of the 3-StPH⁺ + I⁻ complex, the absence of any quenching effect on photoisomerization is probably due to a fortuitous balance of two processes: the rather high ISC yield of the complex ($\Phi_{TE} \sim 0.5$) leads to a complete recovering of the reactive molecules quenched at the S₁ level. Should the reaction in the absence of quenchers proceed at the S₁ level (singlet mechanism), as recently demonstrated for stilbene [9], the last result would imply the same decay ratio from S₁ and T₁ to the two ground state isomeric forms.

The reported effects offer an interesting and useful way of inducing isomerization by external heavy atoms in very little photoreactive stilbene-like molecules.

Acknowledgements

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References

- 1 A. R. Gutiérrez and D. G. Whitten, *J. Am. Chem. Soc.*, **96** (1974) 7128.
- 2 G. Bartocci, P. Bortolus and U. Mazzucato, *J. Phys. Chem.*, **79** (1975) 21.
- 3 A. R. Watkins, *J. Phys. Chem.*, **78** (1974) 1885, 2555.
- 4 G. Bartocci, P. Bortolus and G. Favaro, in preparation.
- 5 G. Favaro, U. Mazzucato and F. Masetti, *J. Phys. Chem.*, **77** (1973) 601.
- 6 G. Beggiano, G. Favaro and U. Mazzucato, *J. Heterocycl. Chem.*, **7** (1970) 583.
- 7 See also G. G. Aloisi, U. Mazzucato and L. Minuti, *J. Am. Chem. Soc.*, submitted.
- 8 D. G. Whitten and M. T. McCall, *J. Am. Chem. Soc.*, **91** (1969) 5097.
- 9 J. B. Birks, *Chem. Phys. Lett.*, **38** (1976) 437 and references therein.