EXCITED STATE REACTIVITY OF AZA-AROMATICS. VII: PRODUCTION AND QUENCHING OF TRIPLET NAPHTHYL-PYRIDYLETHYLENE INDUCED BY HALIDE ANIONS

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Summary

The effect of alkali halides on the fluorescence and *trans* → *cis* photo-isomerization of 1-(β-naphthyl),2-(4-pyridyl)ethylene in the protonated form has been investigated. The results are compared with those obtained for azastilbenes. In contrast to the effect observed for the latter compounds, both the fluorescence and photoisomerization quenching efficiency follow the order of the oxidation potentials of the anions ($Cl^- < Br^- < I^-$). With the weaker perturber, the photoreaction is enhanced by induction of $S_1 \rightarrow T_1$ intersystem crossing. In the case of the heavier perturbers, the parallel induction of $T_1 \rightarrow S_0$ intersystem crossing leads to a reduction of the overall reaction yield. The analysis of the results obtained gives information on the inherent properties of the excited naphthylpyridylethylenes.

1. Introduction

In previous papers [1, 2] we have reported the effect of inorganic anions on the fluorescence quantum yield ϕ_F and the *trans* → *cis* photo-isomerization quantum yield ϕ_C of protonated *trans*-azastilbenes in fluid solution at room temperature. The compounds studied were characterized either by a relatively high value of ϕ_C, as in the styrylpyridines (StPs), or by a high $S_1 \rightarrow S_0$ internal conversion quantum yield ϕ_{IC}, as in 4'-OCH$_3$-3-StP and 1,2-di(3-pyridyl)-ethylene (3,3'-DPE). Alkali halides were used as quenchers; the halide anions displayed a noticeable quenching effect on the first excited singlet state S_1 of the protonated azastilbenes through a mechanism in which both the negative charge and high atomic number (heavy atom effect) of the halide ion probably play a role. The Stern–Volmer (SV) fluorescence quenching coefficient K_Q increased in the order $Cl^- < Br^- < I^-$. The SV photoisomerization quenching coefficient K_Q^C was equal to K_Q for quenching by Cl^- anions, but it was lower than K_Q for 3-StPH$^+$ with the heavier Br$^-$ and I$^-$ ions, and it was negative in the case of 4'-OCH$_3$-3-StPH$^+$ and 3,3'-DPEH$_2^{++}$,
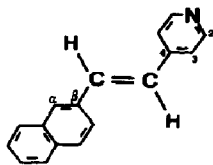
Fig. 1.

indicating an enhancement rather than a quenching of ϕ_C. This was explained by the formation of a complex (probably of charge transfer (CT) nature) between the protonated azastilbene and the halide anion, and by $S_1 \rightarrow T_1$ intersystem crossing (ISC) in the olefin induced by the heavy atom effect [1, 2].

It was considered interesting to investigate this effect in related molecules containing the naphthyl group, such as the naphthylpyridylethylenes (NPE's) [3 - 5], whose photochemical and photophysical behaviour had given some evidence of a higher inherent ISC yield.

This paper reports the results obtained from a study of the fluorescence and photoisomerization quenching by halides of protonated 1-(β-naphthyl), 2-(4-pyridyl)-ethylene (β,4-NPEH$^+$) and the information obtained from a comparison of the kinetic analysis with previous results for 3-StPH$^+$ [1, 2]. The striking behaviour of the naphthyl derivative, which is in apparent contrast with that observed for azastilbenes, confirms the importance of the triplet path in the deactivation of the electronically excited NPE's, mainly in the presence of halide anions but even in their absence.

2. Experimental

The compound investigated in the *trans* form (Fig. 1) was synthesized by standard methods described in previous work [3]. The fluorescence and *trans* → *cis* photoisomerization quenching was studied as reported in a previous paper [2]. The measurements were performed on the protonated species in 80 vol.% water–20 vol.% ethanol at pH 2 in Britton buffers (the pK_a for β,4-NPE is 5.23) [6]. The ionic strength was kept constant at $\mu = 1$ using NaClO$_4$.

3. Results and discussion

3.1. Quantum yields

Compared with stilbene and StPs, styrylnaphthalenes (StNs) [4] and NPEs [3] are characterized by higher fluorescence quantum yield ϕ_F and lower *trans* → *cis* photoisomerization quantum yield ϕ_C in an inert solvent. However, the differences are negligible in an acidic medium where the two
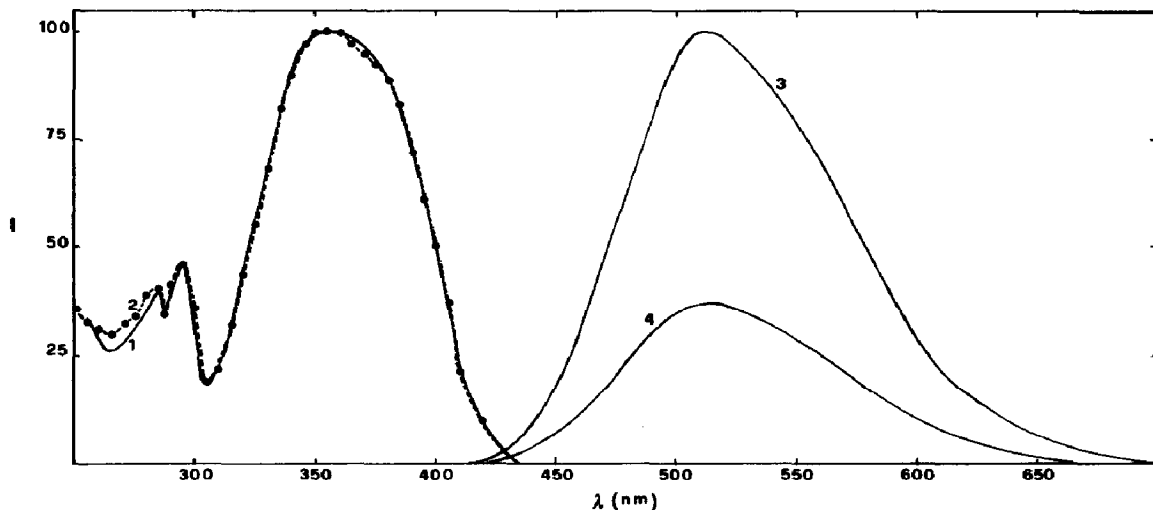
Fig. 2. Absorption (1, ———), fluorescence excitation (2, ······) and fluorescence (3) spectra of β,4-NPEH$^+$ in 80 vol.% water–20 vol.% ethanol at pH 2. Spectrum 4 refers to the fluorescence quenched by 0.15 M NaI.

typical substrates compared in this paper, 3-StPH$^+$ and β,4-NPEH$^+$, have practically the same inherent quantum yields in the absence of perturbers (see first two columns of Table 2). The fact that oxygen has a negligible influence on ϕ_F while it decreases ϕ_C indicates a higher ISC yield for the naphthyl derivatives compared with the azastilbenes. The assumption of a higher triplet yield for NPEs [3] is well confirmed by the investigation of the quenching effect of halide anions.

3.2. Spectra

The absorption spectrum of β,4-NPE presents a low intensity band of naphthalenic type (λ_{max} = 355 nm) which appears on the long wavelength side of an intense stilbene-like band (λ_{max} = 320 nm). The 0–0 transition of the naphthalenic band coincides with the onset of the fluorescence, which is thus assigned to a transition localized in the naphthyl group. Unlike 3-StP [7] and β-StN [4, 8] but like stilbene [7], β,4-NPE has a fluorescence excitation spectrum which is the replica of the absorption spectrum. In an acidic medium the two absorption bands coalesce and only a broad intense band is observable which is shifted towards longer wavelengths (λ_{max} = 360 nm). Figure 2 shows the absorption and fluorescence excitation spectra of trans-β,4-NPEH$^+$ in water–ethanol and its fluorescence spectrum in the absence of quencher and in the presence of NaI (0.15 M). Again the fluorescence excitation spectrum is practically a replica of the absorption spectrum. The fluorescence has a maximum at 515 nm. The large Stokes shift with respect to the absorption implies that the emitting state is here different from the S$_1$ state reached by absorption.

TABLE 1

Quantum yields of fluorescence ϕ_F and *trans* → *cis* photoisomerization ϕ_C of *trans*-β,4-NPEH$^+$ as a function of [Q] in 80 vol.% water–20 vol.% ethanol (see eqn. (2))

| Q	[Q] (M)	ϕ_F	ϕ_F^0/ϕ_F	ϕ_C	ϕ_{CM}	ϕ_{CE}
Cl$^-$	0.00	0.200	1.00	0.300	0.300	0.00
	0.20	0.194	1.03	0.306	0.291	0.0147
	0.40	0.191	1.05	0.327	0.286	0.041
	0.60	0.187	1.07	0.337	0.280	0.056
	0.80	0.185	1.08	0.357	0.277	0.079
	1.00	0.180	1.11	0.360	0.270	0.090
Br$^-$	0.00	0.200	1.00	0.300	0.300	0.00
	0.20	0.137	1.46	0.285	0.205	0.080
	0.40	0.113	1.77	0.267	0.169	0.098
	0.60	0.086	2.32	0.268	0.129	0.139
	0.80	0.070	2.86	0.260	0.104	0.156
	1.00	0.049	4.08	0.251	0.073	0.178
I$^-$	0.00	0.200	1.00	0.300	0.300	0.00
	0.15	0.074	2.70	0.208	0.111	0.097
	0.23	0.048	4.17	0.175	0.072	0.103
	0.35	0.027	7.40	0.144	0.040	0.104
	0.46	0.017	11.80	0.127	0.025	0.102
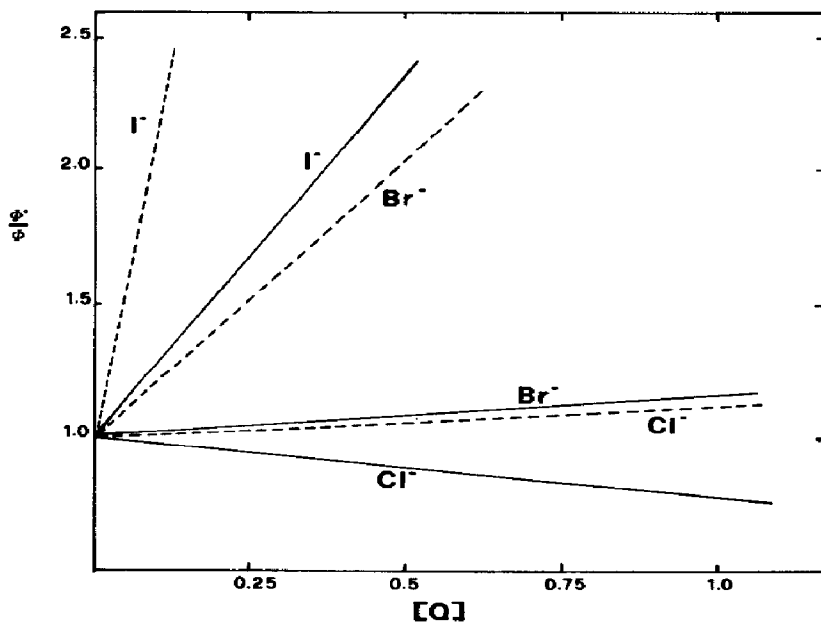
Fig. 3. SV plots for fluorescence (· · · · ·) and *trans* → *cis* photoisomerization (———) of β,4-NPEH$^+$ in the presence of halide anions in 80 vol.% water–20 vol.% ethanol.

Quantum yields and quenching parameters from SV plots of fluorescence and photo-isomerization of *trans*-β,4-NPEH$^+$ in the presence of halides in 80 vol.% water–20 vol.% ethanol compared with similar data for *trans*-3-StPH$^+$

Compound	Quencher										
	None		Cl$^-$			Br$^-$			I$^-$		
	ϕ_F^0	ϕ_C^0	K_Q	i/s	ϕ_C^{lim}	K_Q	i/s	ϕ_C^{lim}	K_Q	i/s	ϕ_C^{lim}
3-StPH$^+$ [a]	0.20	0.27	6.0	—	—	18.8	18.1	0.045	39.0	38.2	0.25
β,4-NPEH$^+$ [b]	0.20$_5$	0.29	0.14	0.20	0.59	2.12	2.10	0.255	11.3	13.0	0.145

[a]From ref. 2; [b]λ_{ex} = 336 nm.

3.3. Quenching experiments

Figure 3 shows the SV plots for fluorescence and photoisomerization in the presence of the three quenchers. Table 1 reports the quantum yields of fluorescence and photoisomerization of β,4-NPEH$^+$ in water–ethanol as a function of the halide concentration. The main results are collected in Table 2 where the corresponding parameters for 3-StPH$^+$ are also reported for comparison [2]. Taking τ_F = 1.3 ns for the fluorescence lifetime of β,4-NPEH$^+$ [6], it is found that only with I$^-$ as quencher does the quenching rate parameter $k_Q = K_Q/\tau_F \approx 9 \times 10^9$ M^{-1} s^{-1} reach the diffusional value in water–ethanol at room temperature. A similar result was found for 3-StPH$^+$ (τ_F = 5.5 ns) for which again k_Q reaches the diffusional value only by interaction with the iodide anion. The K_Q coefficients obtained from the SV plots for fluorescence quenching by the three anions follow the same order for both molecules (Table 2) but the absolute values are smaller for the naphthyl derivative. This is not only due to its shorter lifetime (a factor of about 4 less than that for 3-StPH$^+$) but also depends on the excited partner if we consider that K_Q for (β,4-NPEH$^+$ + Cl$^-$) is 40 times less than K_Q for (3-StPH$^+$ + Cl$^-$).

The SV plots for the isomerization quenching of β,4-NPEH$^+$ lead to interesting results. Even in this case [2] their slopes with Br$^-$ and I$^-$ are smaller than the fluorescence plots but the efficiency of the quenchers is reversed. For the 3-StPH$^+$ photoreaction, which is assumed to occur in the S$_1$ manifold [1], the quenching efficiency by I$^-$ is a minimum (no quenching at all), whereas for the β,4-NPEH$^+$ photoreaction it has a maximum value. Instead, the quenching efficiency by Br$^-$ for the photoreaction of β,4-NPEH$^+$ is markedly reduced compared with fluorescence and a noticeable enhancement of ϕ_C is observed with Cl$^-$.

The experimental data show that the interaction between the excited molecule and the anion offers an alternative way of populating the triplet manifold through an enhanced ISC by the heavy quenchers. The quenching of S$_1$ is thus more or less compensated by the molecules which reach T$_1$

through the olefin–anion interaction [1, 2]. As in the case of the 4'-Br and 4'-I derivatives of 3-StPH$^+$ [1] and in contrast to stilbene [9], the NPEs have a relatively high inherent ISC yield, so that the maximum T_1 population through the complex is already obtained in the presence of the weak S_1 quencher Cl$^-$. With the heavier quenchers Br$^-$ and I$^-$ there is a net decrease of the overall T_1 population because the olefin–anion interaction in the T_1 manifold favours the $T_1 \to S_0$ ISC avoiding the isomerization.

3.4. Analysis of the photoisomerization quenching

Following the reaction scheme and kinetics reported previously [2, 4], only the slope of the fluorescence SV plot gives directly the quenching constant $K_Q = k_Q \tau_F$ of the uncomplexed molecule ^{1}M*. However, the photoreaction SV plot has a different slope for most cases and it often deviates from linearity from the start of the reaction [2, 4]. In fact, the experimental photoreaction yield ϕ_C is at any [Q] the sum of the quantum yield ϕ_{CM} of the fraction of molecules which do not interact with Q and the quantum yield ϕ_{CE} of the fraction of molecules which react through the complex E. ϕ_{CE} can be easily calculated (last column of Table 1) from the difference between the experimental value and the inherent yield calculated from the SV coefficient of the fluorescence plots:

$$\phi_{CE} = \phi_C - \phi_{CM} = \phi_C - \frac{\phi_C^0}{1 + K_Q[Q]} \tag{1}$$

From the photostationary state kinetics it can be seen [2] that

$$\frac{1}{\phi_{CE}} = \frac{1}{\phi_C^{\text{lim}}} + \frac{1}{\phi_C^{\text{lim}} K_Q[Q]} \tag{2}$$

where the reaction yield ϕ_C^{lim} induced by the complex refers to [Q] $\to \infty$. The intercept/slope i/s ratios of the plots of $1/\phi_{CE}$ against $1/[Q]$, following eqn. (2), should equal the SV coefficients K_Q obtained from the slopes of the SV plots for fluorescence quenching. This was in fact found within experimental error (see Fig. 4 and Table 2).

A confirmation of the reliability of these results comes from the linear plots of $\phi_C \phi_{FM}^0 / \phi_C^0 \phi_{FM}$ against [Q], which give an intercept of 1 and a gradient of $K_Q \phi_C^{\text{lim}} / \phi_C^0$ [4]. The limiting values of the induced yield thus obtained are always equal to those in Table 2 obtained from eqn. (2).

By assuming that the trans → cis photoisomerization of β,4-NPEH$^+$ takes place in the triplet manifold and considering that the ϕ_C value of triplet azastilbenes and their protonated cations is about 0.55 (as was found in several cases by measurements of ϕ_C and photostationary state compositions in the presence of high energy triplet excitation donors [3, 10]) it can be calculated that the inherent $S_1 \to T_1$ ISC yield is $\phi_C^0/0.55 \approx 0.55$ for β,4-NPEH$^+$. In the presence of the weakest perturber, Cl$^-$, the limiting triplet yield increases and approaches unity. Thus it can be reasonably assumed, with Br$^-$ and I$^-$, that the difference between the expected ϕ_C^{lim} value (0.55) and that actually obtained (Table 2) is due to the competition by the $T_1 \to S_0$
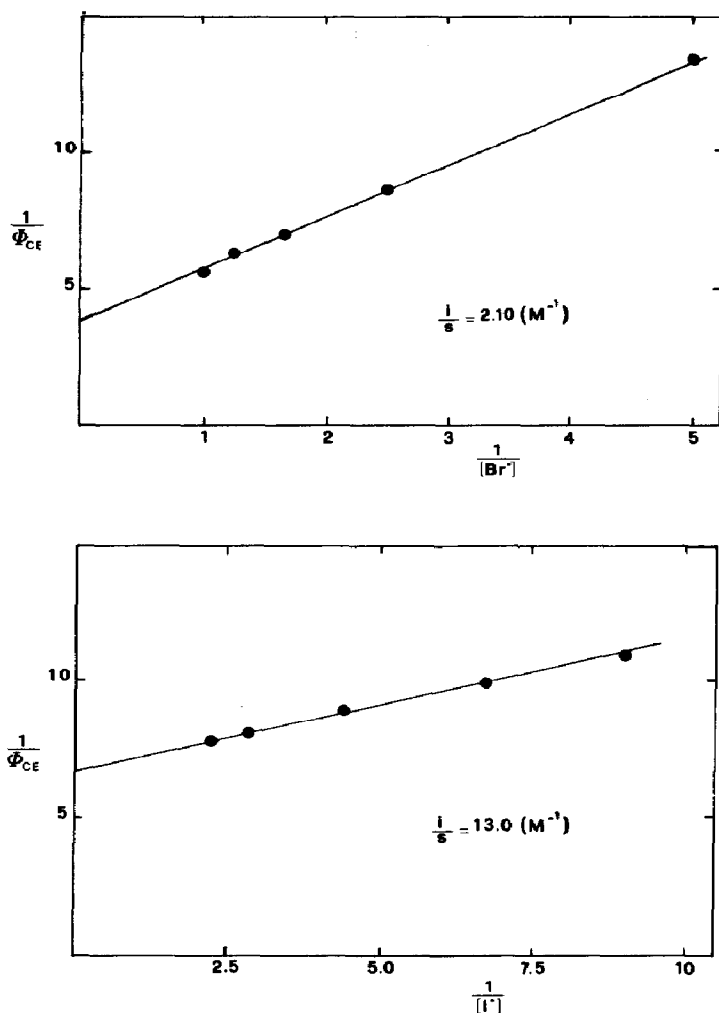
Fig. 4. SV-type plots for *trans* → *cis* photoisomerization of β,4-NPEH$^+$ induced by heavy halide anions in 80 vol.% water–20 vol.% ethanol at pH 2, following eqn. (2).

ISC yield ϕ'_{ISC} induced by the heavy atoms, which can therefore be evaluated:

$$\phi'_{ISC} = 1 - \phi_C^{lim}/0.55 = 0.54 \text{ and } 0.74$$

for the complexes with Br$^-$ and I$^-$ respectively.

This behaviour is analogous to that found for the 4'-Br and 4'-I derivatives of 3-StPH$^+$ [1] which also have limiting induced yield lower than the unsubstituted compound and decreasing with increase of the substituent mass.

A more detailed and complete review and re-elaboration of published and unpublished data of the quenching and induction of photoisomerization of stilbene-like molecules by inorganic anions and other quenchers in organic solvents and in water at different pH values will appear in a later paper.

These results show how we can control the photoisomerization rate of stilbene, azastilbenes and their analogues by the right choice of the perturber.

Acknowledgments

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