

ROLE OF CHARGE TRANSFER INTERACTIONS IN PHOTOREACTIONS

III: INORGANIC ANION-INDUCED INTERSYSTEM CROSSING OF STILBENE-LIKE MOLECULES[†]

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Summary

The effect of halide and thiocyanate anions on the fluorescence and photoisomerization of *trans*-stilbene, styrylnaphthalenes and their mono-substituted aza analogues was studied in a 2:3 acetonitrile:water mixture. The quenching of the fluorescence depends on the oxidation potential of the perturbers and is generally accompanied by anion-induced population of the reactive triplet state of the fluorescers. The limiting induced quantum yield for the *trans* → *cis* photoisomerization in the triplet manifold reaches its maximum value of about 0.5 for the iodide anion which has the best heavy atom and electron donor properties.

1. Introduction

Electron donors (or acceptors) and heavy atom perturbers have been used effectively in recent years to induce triplet photoisomerization of ethylenic compounds [1 - 7].

In our previous study of the interaction of inorganic anions X^- with stilbene-like molecules M^* excited in the S_1 singlet state and of the effect of this interaction on the photoisomerization mechanism [5 - 7], the measurements were carried out in acidic solutions since the protonated species are better electron acceptors than the neutral molecules are. Information on the interaction of the anions with free bases is now sought, and their behaviour is compared with that reported for systems where aliphatic and aromatic amines act as electron donors towards M^* [1, 2]. The interaction of M^* with X^- is believed to have a charge transfer (CT) character even though there is no spectroscopic evidence for this [5 - 11]. The interesting aspect of using

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inorganic anions as donors is that the weak complexes that they form with the excited olefins are short lived and do not fluoresce [11]. Therefore they are potentially suitable for inducing radiationless transitions, such as internal conversion (IC) and intersystem crossing (ISC), in the acceptors. ISC is particularly efficient when the anion has a high atomic weight. As stilbene-like molecules can isomerize in both singlet and triplet states [12, 13], an increase in the triplet population by suitable additives can produce a substantial increase in the photoreaction quantum yields of compounds with low inherent yields [3, 6]. It should be recalled that, once M^* reaches the T_1 level, rapid equilibration is assumed to occur from the 3trans isomer to the twisted 3perp isomer, which in turn decays to approximately equal fractions (0.5) of the ground state 0trans and 0cis isomers [12].

In this paper we report the results obtained from a study of the fluorescence and photoisomerization quenching of stilbene (St), styrylnaphthalenes (StN's) and some aza analogues, namely styrylpyridines (StP's) and naphthylpyridylethylenes (NPE's), by halide and thiocyanate anions in a 2:3 acetonitrile:water mixture. Some interesting information on the induced photoreaction mechanism is also reported.

2. Experimental details

The ethylenic compounds were synthesized for previous work and their preparation is described elsewhere [14]. In the notation for the naphthyl derivatives (Fig. 1) the isomeric positions of the naphthyl group and the pyridyl group with respect to the ethylenic bridge are indicated by Greek letters and numbers respectively.

The sodium and potassium salts (RP grade) used as fluorescence quenchers and the acetonitrile (RS grade) were obtained from Carlo Erba SpA.

The fluorescence measurements were made using a Perkin-Elmer MPF-44 spectrophotofluorimeter with a rhodamine B accessory for spectrum correction. For the quenching measurements, the olefin concentration was in the range $(1 - 3) \times 10^{-5}$ M and the anion concentration was varied up to 1 M or, in some cases, 1.5 M. Further details are given in previous papers [1, 2].

The *trans* \rightarrow *cis* photoisomerization quantum yields ϕ_C were determined spectrophotometrically by irradiation at 325 nm using an Osram XBO 150 W

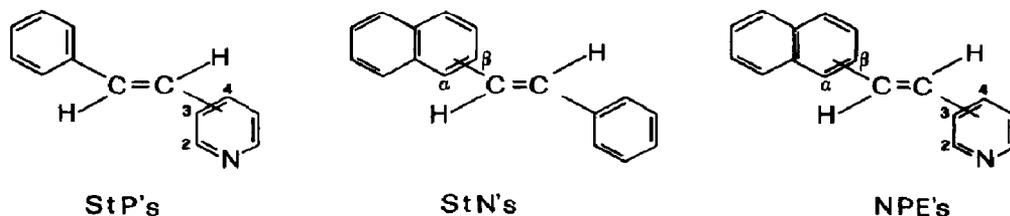


Fig. 1. The compounds used in this study.

xenon lamp coupled to a Hilger–Watts D-292 grating monochromator. The olefin concentration was of the order of 10^{-4} M. The conversion percentage was held below 10% to avoid competition from the back photoreaction. Since the formation of triplet molecules (and hence of the isomerized product) is catalysed by dissolved oxygen, all measurements were performed in solutions which had been deaerated by bubbling nitrogen through them.

3. Results and discussion

3.1. Fluorescence quenching

The absorption spectra of the stilbene-like compounds M showed no evidence of ground state interactions in the presence of simple diamagnetic inorganic anion quenchers ($Q \equiv X^-$), at least up to $[X^-] = 1$ M. The fluorescence intensity of *trans*-M in a 40:60 (by volume) acetonitrile:water mixture was quenched with an efficiency which increased with decreasing X^- ionization potential (Fig. 2), indicating the formation of a CT-stabilized complex. Linear Stern–Volmer (SV) plots were obtained from the usual equation

$$\phi_{FM}^0 / \phi_{FM} = 1 + K_Q[Q] = 1 + k_Q\tau_M[Q] \quad (1)$$

where the ratio of the quantum yield in the absence of Q to that in the presence of Q is equated to the intensity ratio at the wavelength of the analysis. The plots gave quenching coefficients K_Q (see Table 1) that were reproducible to within 5%, with the exception of the weakest complexes ($K_Q < 1$) where the error could be as much as 50%. High SV coefficients were obtained only with the relatively longer lived β -StN and $\beta,3$ -NPE acceptors and the most efficient I^- quencher as donor. Downward curvature from the

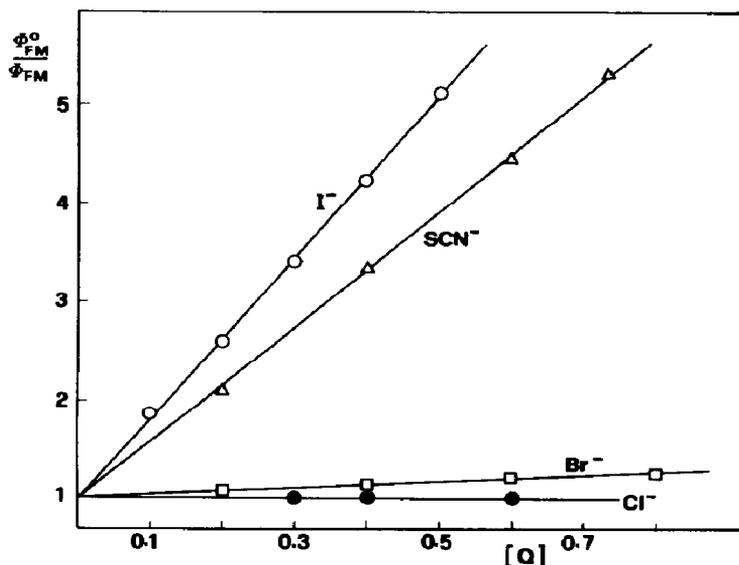


Fig. 2. SV plots for the fluorescence quenching of $\beta,4$ -NPE in a 2:3 acetonitrile:water mixture by anions with different oxidation potentials.

TABLE 1

Stern-Volmer coefficients K_Q for the quenching of some excited stilbene-like molecules by inorganic anions and the *trans* \rightarrow *cis* photoisomerization quantum yields of complexes in a 2:3 acetonitrile:water mixture compared with the inherent fluorescence and photo-reaction quantum yields of the acceptors

M^*	X^-	ϕ_{FM}^0 ^a	ϕ_C^0	K_Q (eqn. (1)) (M^{-1})	ϕ_{CE}^{lim} (eqn. (3))	$K_Q(i/s)$ (eqn. (3))	ϕ_{CE}^{lim} (eqn. (4))
St ^b	I ⁻	0.015	0.43	(2.0)	≈ 0.3	≈ 3.0	(0.3)
	SCN ⁻			(0.4)	≈ 0.0		≈ 0.0
2-StP	I ⁻	0.001	0.41	0.4	0.25	0.4	0.23
	SCN ⁻			0.1 ₅	0.13	0.2 ₅	0.18
3-StP	I ⁻	0.029	0.44	4.25	0.52	3.9	0.51
	SCN ⁻			2.3	0.25	3.1	0.29
4-StP	I ⁻	0.001	0.42	0.4	0.30	0.1	0.20
α -StN	I ⁻	0.25	0.29	4.6	0.28	4.6	0.28
β -StN	I ⁻	0.51	0.19	49.0	0.48	45.0	0.47
	SCN ⁻			6.4	0.37	6.9	0.37
β ,2-NPE	I ⁻	0.09	0.36	7.5	0.52	8.6	0.55
β ,3-NPE	I ⁻	0.51	0.14	40.0	0.39	33.0	0.37
	SCN ⁻			22.0	0.30	20.0	0.30
β ,4-NPE	I ⁻	0.11	0.34	8.0	0.48	6.6	0.45
	SCN ⁻			6.0	0.34	6.4	0.35
	Br ⁻			0.3	0.55	0.2 ₄	0.52
	Cl ⁻			0.05			

^aThe values for the StPs are taken from ref. 15 ($\lambda_{ex} = 320$ nm) and those for the StNs are taken from ref. 1 ($\lambda_{ex} = 350$ nm); the values for St and the NPEs are from the present work ($\lambda_{ex} = 324$ nm; solvent, acetonitrile).

^bThe values in parentheses were obtained from the initial slopes of non-linear SV plots.

beginning was obtained only in the plot for the St acceptor. Although the reason for this behaviour is not clear, it may be related to the controversial existence of two fluorescence decay components with different weights and lifetimes [2] (see below). In contrast with the case of quenching by amines [1, 2], no exciplex fluorescence was observed with the present systems. This was expected from both the polarity of the solvent used and the fact that the complexes formed between singlet excited aromatic molecules and inorganic anions are known to be very short lived [11]. The CT nature of these exciplexes, and in particular the importance of the proximity of the CT level to S_1 for their efficient formation [9], seems to be established even though no evidence for a complete electron transfer reaction from X^- to M^* has been obtained [8]. The exciplex can thus be considered to be an encounter complex M^*X^- with enough CT character to undergo fast ISC [8 - 11], especially when X is a heavy atom or possibly when M has a high inherent ϕ_{ISC}^0 [2].

3.2. Quenching rate parameters

It is necessary to know the fluorescence lifetime τ_M of the acceptors in order to calculate the rate parameters k_Q from the SV coefficients (eqn. (1)). However, the τ_M values for the StPs have been estimated by quenching experiments to be well below 1 ns and thus are not directly measurable by conventional fluorimeters [13]. A lifetime of about 0.1 ns has been reported for St in the recent literature [16]. As in the case of the amine quenchers [2], the value of k_Q (about $2.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ when $Q \equiv I^-$) obtained from the initial slope of the non-linear SV plot for the quenching of St, which is expected to act as a weaker electron acceptor than the other acceptors investigated [2], is too high. A contribution from non-diffusional (static or dynamic) quenching [17], in view of the very short τ_M , cannot offer an explanation of the high quenching efficiency since a downward rather than an upward deviation from linearity was observed. This curvature could be related to the occurrence of another longer decay component (1.5 ns) [18], although such decay is still a matter of controversy since several laboratories have failed to observe it [2]. Its presence would imply the existence of differential quenching dependent on the relative weight of the two components [19, 20].

In general the naphthyl derivatives have longer lifetimes than the phenyl analogues. Moreover naphthalene has a greater electron affinity than benzene (ref. 17, pp. 462 - 464). Therefore these olefins are expected to be better electron acceptors than stilbenes are. In fact, rather higher SV coefficients were obtained. The value of τ_M for these compounds in acetonitrile-water mixtures was estimated by the effect of oxygen on the fluorescence. Two exponential decay components have been found for β -StN [19, 20] and its aza analogues [21] in non-polar solvents and have been assigned to conformeric species. Analysis of differential quenching is outside the scope of this paper as observations of fluorescence as a function of both excitation and emission wavelengths are required [20]. However, the fact that linear SV plots were obtained in all cases except for St indicates that the effective τ_M for quenching is a weighted average of the two components. It is also possible that one of the two components predominates at the wavelengths and/or [Q] ranges employed or that the conformers have similar lifetimes in the solvent used in this work. A combination of both situations could also apply. It is therefore preferable to use the average value of τ_M obtained from the oxygen quenching of fluorescence at fixed $\lambda_{ex} = 325 \text{ nm}$ and $\lambda_{em} = 380 \text{ nm}$, assuming a diffusional rate constant k_{O_2} of $1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ and an $[O_2]$ value of $8 \times 10^{-4} \text{ M}$ in the air-equilibrated mixed solvent. These values were obtained for the mixed solvent at 25 °C by the interpolation of viscosity ($k_{diff} = 8RT/3000\eta$) and $[O_2]$ data reported for water and acetonitrile in ref. 22. The results for the naphthyl derivatives are shown in Table 2 for systems where the quencher is I^- . Only the k_Q values of the aza compounds approach the diffusional value. In fact the presence of the heteroatom makes them stronger electron acceptors, as found in the systems formed by NPEs and amines [2]. The corresponding hydrocarbons (StNs)

TABLE 2

Lifetimes and Stern–Volmer rate parameters for the fluorescence quenching of styrylnaphthalenes and related molecules by I^- in 2:3 acetonitrile:water mixtures

M^*	$K_Q (M^{-1})^a$	$\tau_M (ns)$	$k_Q (\times 10^9 M^{-1} s^{-1})$
α -StN	4.6	1.9	2.4
β -StN	47.0	12.5	3.8
$\beta,2$ -NPE	8.0	1.1	6.8
$\beta,3$ -NPE	37.0	3.8	10.5
$\beta,4$ -NPE	7.3	0.9	8.1

^aAverage of the two values reported in Table 1.

have sensibly lower k_Q values, particularly when the styryl group is attached at the α position of the naphthyl ring. Smaller k_Q values are obviously expected when less efficient quenchers than I^- are used since the components of the encounter complex may separate partially without interacting.

3.3. Induced photoisomerization

The *trans* \rightarrow *cis* photoisomerization of M^* was studied in parallel with the investigation of fluorescence quenching. The spectral behaviour at different irradiation times indicates that isomerization is the only photoreaction to be accounted for at low conversion percentages (below 10%). Complications due to the photoaddition reaction of singlet stilbene-like molecules (observed with alkenes [23] and amines [24]) can be avoided by using an inorganic anion as quencher; in any case, this reaction has a much smaller quantum yield than that of photoisomerization. The ϕ_C values in Table 1 are averages of at least three independent experiments with a mean deviation of 8%.

The photoreaction was quenched less than fluorescence and even enhanced in most cases. This means that the complex itself can contribute to isomerization, probably by the formation of the reactive triplet state of the olefin. Figure 3 shows, as an example, the SV plots of ϕ_C^0/ϕ_C versus $[Q]$ for $\beta,3$ -NPE with two quenchers. It should be noted that triplet aromatics, but no radical anions, have been detected as intermediates in flash photolysis experiments on related systems [8, 10]. This seems to rule out a photoisomerization mechanism through the formation of the olefin negative ion. In fact a radical mechanism has been neglected even with amine quenchers [1, 2], since the quantum yield of induced photoisomerization decreased markedly in polar solvents where radical formation should be favoured.

At any $[Q]$ the ϕ_{CE} induced by the complex can be obtained from the difference between the overall observed *trans* \rightarrow *cis* photoisomerization quantum yield ϕ_C and the contribution ϕ_{CM} from the acceptor molecules which react in the monomeric form without interacting with Q ($\phi_{CE} = \phi_C - \phi_{CM}$). ϕ_{CM} can be evaluated from ϕ_C^0 in the absence of Q and K_Q , which in turn is ob-

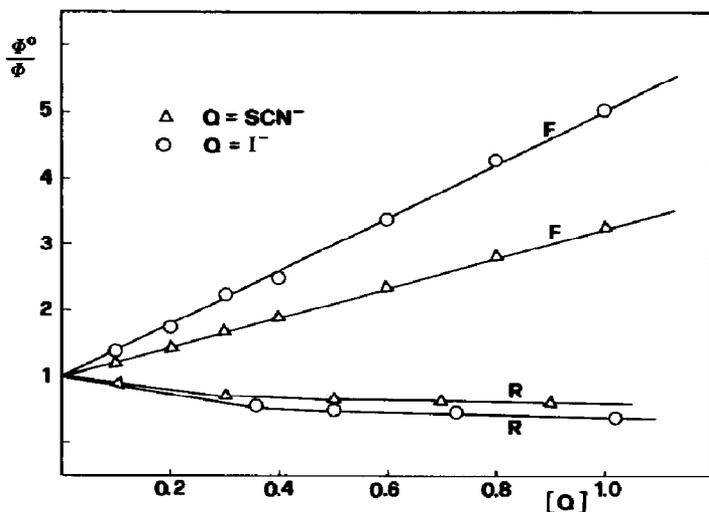


Fig. 3. SV-type plots for fluorescence (F) and photoisomerization (R) quenching of *trans*- β ,3-NPE by SCN^- (Δ) and I^- (\circ) in a 2:3 acetonitrile:water mixture.

tained from fluorescence quenching measurements by using eqn. (1). In fact, regardless of whether M isomerizes in the singlet or the triplet manifold in the absence of an interaction with Q, the inherent photoreaction quantum yield ϕ_C^0 is reduced to ϕ_{CM} by the perturber according to the usual SV relationship (analogous to eqn. (1))

$$\phi_C^0/\phi_{CM} = 1 + K_Q[Q] \quad (2)$$

The results obtained for the systems investigated are collected in Table 1. The SV coefficients K_Q were obtained from independent experiments by measuring the quenching of M fluorescence (Table 1, fifth column) and by determining the intercept-to-slope (i/s) ratios of the plots of $1/\phi_{CE}$ versus $1/[Q]$ (Table 1, seventh column) and using the equation

$$\frac{1}{\phi_{CE}} = \frac{1}{\phi_{CE}^{lim}} + \frac{1}{\phi_{CE}^{lim}K_Q[Q]} \quad (3)$$

where ϕ_{CE}^{lim} is the photoisomerization quantum yield induced by the complex (referred to $[Q] \rightarrow \infty$). The agreement between the two sets of K_Q values is very satisfactory in most cases (the exceptions have been discussed above). Also given in Table 1 are the values of ϕ_{CE}^{lim} obtained from the intercepts of the plots of eqn. (3) or from eqn. (4) which combines both fluorescence and isomerization quenching data [1, 2] (Fig. 4):

$$\frac{\phi_C \phi_{FM}^0}{\phi_C^0 \phi_{FM}} = 1 + K_Q \frac{\phi_{CE}^{lim}}{\phi_C^0} [Q] \quad (4)$$

Here again the two sets of ϕ_{CE}^{lim} values are in very good agreement. Compared with the inherent ϕ_C^0 values, they show either a general enhancement or no effect for isomerization parallel to the fluorescence quenching. Therefore even in the present case the *trans* \rightarrow *cis* photoreaction is quenched at the

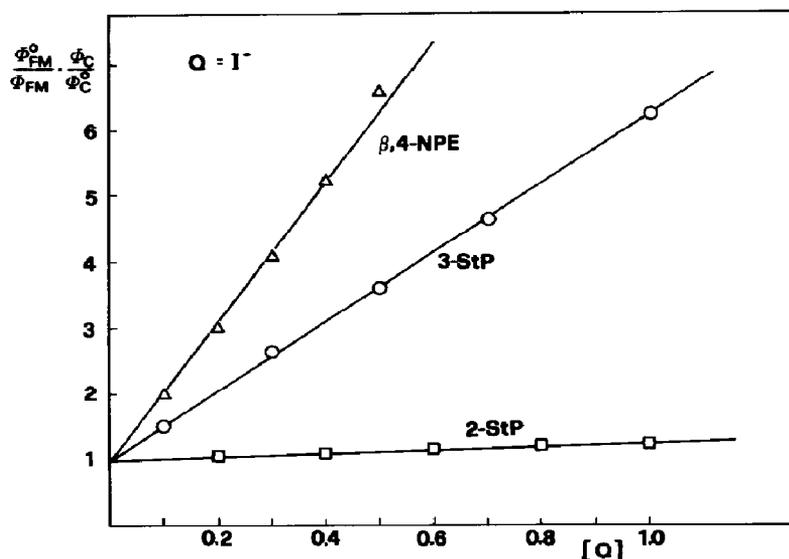


Fig. 4. Linear plots for the quenching of some diarylethylenes by I^- (eqn. (4)).

S_1 level and is almost always induced at the T_1 level. This is in agreement with previous results which showed that CT interactions in the excited state of diarylethylenes may produce the triplet olefin which undergoes geometrical isomerization and thus provides a chemical probe for the detection of triplets [1, 2, 4 - 7]. Generally, higher induced quantum yields were observed with good X^- donors (I^- , SCN^-) than with amines [1, 2] whose complexes have an additional radiative decay.

The results of Table 1 can be separated into two groups. The first group consists of monomers with high inherent isomerization quantum yields (about 0.5) and low inherent emission yields (less than 0.1), and includes St and the StPs. These compounds are also characterized by negligible ISC quantum yields, at least in fluid solvents at room temperature, so that the photoreaction in the absence of X^- is believed to occur by internal rotation in the singlet manifold [12, 13]. The triplet yields of these compounds remain relatively small even for the complexed form unless a heavy atom is present in the complex. Hence it is of interest to observe that SCN^- , which is only a slightly less efficient fluorescence quencher than I^- , does not lead to triplet population and hence to induced isomerization in the case of St, or to noticeably smaller induction compared with the values of ϕ_C^0 and ϕ_{CE}^{lim} obtained with I^- in the case of 2-StP and 3-StP. In contrast, the effect of I^- on 3-StP is to induce a ϕ_{ISC}^{lim} value of about unity which leads to a limiting induced photoreaction quantum yield of approximately 0.5 (considering that the triplet fraction which goes to the *trans* and the *cis* ground states is about 0.5 in practice) [12, 13]. The behaviour of 2-StP and 4-StP appears to depart from this pattern. Even if the emission measurements are uncertain for these poorly fluorescent molecules, their photoreaction quantum yields are reliable and give ϕ_{CE}^{lim} values that are rather less than 0.5 even with I^- .

It should be noted that these two isomers, in which the heteroatom is in the *ortho* and *para* position with respect to the ethylenic bridge, appear to be characterized by non-negligible IC to S_0 [13] which may also offer an important contribution to the deactivation of the complex.

The second group includes monomers with high inherent emission yields such as the β -naphthyl derivatives, particularly β -StN and $\beta,3$ -NPE (for which $\phi_{FM}^0 \approx 0.5$ and consequently ϕ_C^0 is smaller). Here the quenching of the radiative process leads to the recovery of a larger number of quanta for radiationless deactivation. Therefore the induced photoreaction yield (about 0.4) is appreciably larger than the inherent photoreaction yield (about 0.15). A net increase was also found for the $\beta,2$ and $\beta,4$ isomers, although this effect was less marked because of the smaller value of ϕ_{FM}^0 and the larger value of ϕ_C^0 even in the absence of perturbers. The indication of an important $S_1 \rightarrow T_1$ ISC in the molecules containing the naphthalene moiety [1, 25] receives indirect support from the results for $\beta,4$ -NPE where the value of ϕ_{CE}^{lim} with Br^- is even higher than the value with the heavier I^- perturber. This could be due to the high triplet population in these molecules even with quenchers other than I^- and to partial quenching of T_1 when the quencher is I^- . Such a competitive effect between the $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ ISC induced by I^- has been found for similar systems [7] and cannot be excluded in the present case either. However, it should be noted that the triplet mechanism for direct photoisomerization of β -StN has been questioned in a recent paper [26] in which the results of azulene and oxygen quenching experiments are reported.

3.4. Interaction mechanism

It has been established that the proximity of the CT state (of energy E_{CT}) to the excited state M^* which is to be quenched is a key factor in the quenching of aromatic molecules by inorganic anions [8, 9]. Fast diffusion-controlled quenching takes place when E_{M^*} is greater than E_{CT} but the rate falls rapidly when E_{M^*} is equal to E_{CT} or less [9]. The energies of the CT levels for $M-X^-$ pairs can be roughly evaluated [8 - 10] from the differences between the oxidation potential of the anions and the reduction potential of M :

$$E_{CT} = E(X^-/X) - E(M/M^-) \quad (5)$$

$E(M/M^-)$ is identified by the half-wave polarographic potential $E_{1/2}^{red}$. Unfortunately the reduction potentials of M acceptors for our naphthyl derivatives are not available. When the $E_{1/2}^{red}$ values reported for St [27] and the StPs [28] are used, an approximate evaluation of E_{CT} from eqn. (5) (Table 3) leads to a value of 3.3 ± 0.1 eV for St and 3-StP when Q is I^- or SCN^- and a value of 3.0 ± 0.1 eV for 2-StP and 4-StP with the same quenchers. Since $E_{M^*} \approx 3.75 \pm 0.05$ eV for St and the StPs, an almost diffusional quenching rate ($k_Q \approx 1.1 \times 10^{10} M^{-1} s^{-1}$) should be expected with these two anions. This hypothesis leads to the lifetimes shown in Table 3, sixth column, which are in good agreement with previous estimates [13].

TABLE 3

Half-wave potentials for acceptors, the calculated energies of charge transfer levels for M-X⁻ pairs and the estimated lifetimes for stilbene and the styrylpyridines

<i>M</i>	$-E_{1/2}^{\text{red a}}$ (V (SCE))	$E_{\text{CT}}(\text{eV})^{\text{b}}$		$E_{\text{M}^*}^{\text{c}}$ (eV)	$\tau_{\text{M}}^{\text{d}}$ (ns)
		$X^- \equiv \text{I}^-$	$X^- \equiv \text{SCN}^-$		
St	2.15	3.31	3.41	3.79	
2-StP	1.81	2.97	3.07	3.71	0.04
3-StP	2.08	3.24	3.34	3.75	0.37
4-StP	1.69	2.85	2.95	3.80	0.03

^aTaken from ref. 27 for St in dimethylformamide and from ref. 28 for StPs in a 1:3 water:dioxane mixture.

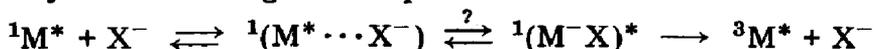
^bCalculated from eqn. (5) using $E^{\text{ox}}(X^-/X)$ (SCE) taken from ref. 29.

^cMeasured as the intersections of normalized absorption and fluorescence spectra in acetonitrile.

^dCalculated from $K_{\text{Q}} = k_{\text{Q}}\tau_{\text{M}}$ assuming a diffusional rate parameter.

When Cl^- is the quencher E_{CT} is much greater than E_{M^*} and the quenching becomes negligible, whilst with a Br^- quencher an intermediate situation is expected.

The photoisomerization results suggest that fluorescence quenching probably occurs through the sequence



where the electron transfer, even if complete, produces a radical ion-radical pair which does not dissociate into separate solvated partners but has a faster rate of radiationless deactivation, mainly through ISC and IC. The deactivation of the complexes with I^- is often entirely due to enhanced $\text{S}_1 \rightarrow \text{T}_1$ ISC, which appears to be faster than dissociation of the complexes either into solvent-separated M^- and X or into M and X^- . A heavy atom effect is not the only factor responsible for this behaviour since SCN^- also induces efficient ISC (with the exception of the complex with St). Not only is the position of the CT state below ${}^1\text{M}^*$ important for the quenching of the fluorophores, but it is also likely that the position of ${}^3\text{M}^*$ below the CT state is important for efficient spin inversion and T_1 population. In fact the CT state may act as a suitable mediator between the two spin manifolds [10]. In conclusion, a tentative interpretation for the observed behaviour is that a CT level between the S_1 and T_1 levels of M^* may represent the ideal situation for efficient quenching of S_1 accompanied by efficient exothermic population of T_1 . The population of T_1 through $\text{S}_1 \rightarrow \text{T}_1$ ISC is thus expected to be favoured when heavy atoms are present in the interacting system and/or the triplet state of the acceptor lies below but not too far from the CT state. Unfortunately this hypothesis is difficult to confirm as very little information is available on the triplet levels of stilbene-like molecules. There are some indications [30] that the $E_{3\text{M}^*}$ values of the StPs are similar to that of

St (2.2 eV) [12]. The similar values of E_{CT} and E_{3M^*} obtained for St and the StPs disagree with the ϕ_{CE}^{lim} values found for St with I^- (they are appreciably lower than that for 3-StP quenched by I^-) and particularly with the value for St quenched by SCN^- (there is no induced isomerization compared with a substantial ϕ_{CE}^{lim} value for 3-StP quenched by SCN^-). Further work is needed to clarify this point. Tentative explanations based on differences between the structures of the complexes with azastilbenes and those with the corresponding hydrocarbons or on the role of the (n,π^*) states introduced by the heteroatom in the ISC of the complexes seem too speculative at this stage. It should also be noted that extrapolation of ϕ_{CE}^{lim} to $[Q] \rightarrow \infty$ can lead to unreliable results when the inherent fluorescence quantum yield is very low (less than 0.01) and the quenching is not accompanied by enough induced isomerization to be accurately measurable at the value of $[Q]$ employed. This could be the case when K_Q is less than 0.5, e.g. with 2-StP and 4-StP quenched by I^- and with St and 2-StP quenched by SCN^- . Relatively high values of $[Q]$ are required to study systems with small K_Q which would introduce complications of various types.

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References

- 1 G. G. Aloisi, U. Mazzucato, J. B. Birks and L. Minuti, *J. Am. Chem. Soc.*, **99** (1977) 6340, and references cited therein.
- 2 G. G. Aloisi, G. Bartocci, G. Favaro and U. Mazzucato, *J. Phys. Chem.*, **84** (1980) 2020.
- 3 A. R. Gutierrez and D. G. Whitten, *Mol. Photochem.*, **9** (1979) 157, and references cited therein.
- 4 F. D. Lewis and J. T. Simpson, *J. Phys. Chem.*, **83** (1979) 2015, and references cited therein.
- 5 P. Bortolus, G. Bartocci and U. Mazzucato, *J. Phys. Chem.*, **77** (1973) 605; **79** (1975) 21.
- 6 G. Bartocci, U. Mazzucato and P. Bortolus, *J. Photochem.*, **6** (1977) 309.
- 7 G. Bartocci, U. Mazzucato and G. Favaro, *J. Photochem.*, **11** (1979) 79.
- 8 A. R. Watkins, *J. Phys. Chem.*, **77** (1973) 1207; **78** (1974) 1885, 2555.
- 9 A. Treinin and E. Hayon, *J. Am. Chem. Soc.*, **98** (1976) 3884.
- 10 H. Shizuka, M. Nakamura and T. Morita, *J. Phys. Chem.*, **84** (1980) 989.
- 11 N. Mataga and M. Ottolenghi, in R. Foster (ed.), *Molecular Association*, Vol. 2, Academic Press, London, 1979, and references cited therein.
- 12 J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton and O. C. Zafiriou, *Org. Photochem.*, **3** (1973) 1, and references cited therein.
- 13 G. Bartocci, F. Masetti, U. Mazzucato and G. Galiazzo, *J. Phys. Chem.*, **84** (1980) 847, and references cited therein.

- 14 G. Galiazzo, *Gazz. Chim. Ital.*, 95 (1965) 1322.
P. Bortolus and G. Galiazzo, *J. Photochem.*, 2 (1974) 361.
G. Galiazzo, P. Bortolus and F. Masetti, *J. Chem. Soc., Perkin Trans. II*, (1975) 1712.
- 15 G. Bartocci and U. Mazzucato, *J. Lumin.*, to be published.
- 16 M. Sumitani, N. Nakashima, K. Yoshihara and S. Nagakura, *Chem. Phys. Lett.*, 51 (1977) 183.
F. Heisel, J. A. Miehe and B. Sipp, *Chem. Phys. Lett.*, 61 (1979) 115.
B. I. Greene, R. M. Hochstrasser and R. B. Weisman, *Chem. Phys. Lett.*, 62 (1979) 427.
- 17 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, New York, 1970, pp. 441 - 447, and references cited therein.
- 18 D. J. S. Birch and J. B. Birks, *Chem. Phys. Lett.*, 38 (1976) 432.
J. R. Taylor, M. C. Adams and W. Sibbett, *Appl. Phys. Lett.*, 35 (1979) 590.
- 19 E. Haas, G. Fischer and E. Fischer, *J. Phys. Chem.*, 82 (1978) 1638.
Yu. B. Sheck, N. P. Kovalenko and M. V. Alfimov, *J. Lumin.*, 15 (1977) 157.
- 20 J. B. Birks, G. Bartocci, G. G. Aloisi, S. Dellonte and F. Barigelletti, *Chem. Phys.*, 51 (1980) 113.
- 21 F. Masetti, G. Bartocci, U. Mazzucato and G. Galiazzo, *Gazz. Chim. Ital.*, to be published.
- 22 S. L. Murov, *Handbook of Photochemistry*, Dekker, New York, 1973, pp. 85 - 87.
- 23 F. D. Lewis, *Acc. Chem. Res.*, 12 (1979) 152, and references cited therein.
- 24 F. D. Lewis and T. I. Ho, *J. Am. Chem. Soc.*, 99 (1977) 7991.
- 25 M. Sumitani, S. Nagakura and K. Yoshihara, *Chem. Phys. Lett.*, 29 (1974) 410.
- 26 J. Saltiel and D. W. Eaker, *Chem. Phys. Lett.*, 75 (1980) 209.
- 27 R. Dietz and M. E. Peover, *Discuss. Faraday Soc.*, 45 (1968) 154.
- 28 J. Chodkowski and T. Giovanoli-Jakubczak, *Rocz. Chem.*, 41 (1967) 373.
- 29 V. M. Berdnikov and N. M. Bazhin, *Russ. J. Phys. Chem.*, 44 (1970) 395.
- 30 D. G. Whitten and M. T. McCall, *J. Am. Chem. Soc.*, 91 (1969) 5097.