

GEOMETRICAL PHOTOISOMERIZATION OF β -STYRYLNAPHTHALENE IN THE PRESENCE OF ELECTRON ACCEPTORS

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Summary

The fluorescence and the *trans* \rightarrow *cis* photoisomerization of β -styrylnaphthalene in the presence of various electron acceptors were investigated in acetonitrile and methylene chloride. The quenching mechanism of the photoexcited β -styrylnaphthalene and the effect of electron acceptors on the isomerization pathway are discussed.

1. Introduction

It is known that exciplexes are often involved in the intermolecular quenching of photoexcited aromatic molecules [1]. In this context a very important problem is that of the role of exciplexes in singlet-triplet intersystem crossing.

Grellman *et al.* [2, 3], in their flash experiments in polar solutions of aromatic hydrocarbons with dicyanobenzene as quencher, have detected the donor and acceptor ionization products and have proposed an electron transfer mechanism for the triplet formation.

Another mechanism has been suggested by Goldschmidt *et al.* [4], in which an "encounter complex" between the photoexcited molecule and the quencher undergoes a radiationless transition to a charge transfer state or to a dissociative locally excited triplet ($^3A^*Q$) which finally yields the triplet $^3A^*$.

Useful information about the exciplex-induced intersystem crossing can be obtained from the effect of electron donor or acceptor quenchers on those photoreactions which are known to occur by a triplet mechanism.

In previous work [5] we have obtained evidence of a triplet mechanism for the direct *cis-trans* photoisomerization of β -styrylnaphthalene and 3-styrylquinoline. Formation of exciplexes between styrylnaphthalenes in the first excited singlet state and amines as electron donors has been observed [6], and their influence on the *cis-trans* photoisomerization of styrylnaphthalenes has been investigated. Exciplexes of *trans*-stilbene with electron donors and acceptors have recently been studied by Lewis and Simpson [7],

and intersystem crossing to yield stilbene triplets has been found to be an important deactivation pathway.

In this work we present our findings on the effect of some electron acceptors on the fluorescence and *trans* → *cis* photoisomerization of β -styrylnaphthalene (β -StN) in acetonitrile and methylene chloride. Benzonitrile (BN), *p*-dicyanobenzene (*p*-DCB), tetracyanothiophene (TCT) and bis-dicyanomethylene-2,2,4,4-tetramethylcyclobutane (TCTMC) were chosen as electron acceptors.

2. Experimental

The *cis* and *trans* isomers of β -StN were obtained by methods described elsewhere [8]. Acetonitrile and methylene chloride, of the highest purity grade, were dried and distilled. BN (EGA Chemie), anhydrided and vacuum distilled, was stored under nitrogen; *p*-DCB (EGA Chemie) was recrystallized from ethanol; TCT and TCTMC were given by Professor C. Pecile and Professor C. Corvaja.

Fluorescence spectra were measured with a Perkin-Elmer MPF-4 spectrofluorimeter. The fluorescence quantum yield ϕ_f of *trans*- β -StN was determined using quinine bisulphate in 1 N H₂SO₄ as standard. Stern-Volmer fluorescence quenching coefficients K_{SV} were determined from the observation of the fluorescence intensity as a function of the acceptor concentration [Q].

The light source used in the irradiations was a stabilized Osram HBO 200 W high pressure mercury lamp equipped with Balzer interference filters to isolate the desired wavelengths.

The *trans* → *cis* photoisomerization was studied spectrophotometrically at various acceptor concentrations and at a fixed concentration of β -StN (approximately 2×10^{-4} M) which ensured total absorption of the incident light. In order to minimize the concomitant photocyclization of the *cis* isomer produced, the percentage of isomerization did not exceed 15%.

The values of the photoisomerization quantum yield were obtained as a mean of at least two series of runs and their reproducibility was $\pm 5\%$. In both fluorescence and photoisomerization studies the excitation was at 335 nm. At this wavelength the acceptors used have negligible absorption. Furthermore, in the range of concentrations employed in our experiments, the absorption spectra reveal no detectable formation of complexes between the acceptors and the ground state β -StN.

In the anthraquinone-sensitized isomerization the irradiations were performed with 410 nm light. In this case the concentration of β -StN was about 5×10^{-3} M. The photostationary compositions, expressed as the ratio [*cis*]/[*trans*] of the concentrations of the two isomers in the photostationary state, were determined by gas-liquid chromatographic analysis according to a previously described procedure [5]. The reproducibility of the data was $\pm 5\%$.

In all experiments the solutions were deaerated by bubbling with nitrogen. The temperature was always 25 ± 1 °C.

Polarographic half-wave reduction potentials of the acceptors were measured with an Amel model 448 three-electrode apparatus. A saturated solution of Ag-AgCl-tetramethylammonium chloride in acetonitrile was used as the reference electrode and a platinum foil was used as the counter-electrode. Potential sweep voltametry with a hanging mercury drop electrode showed that the reduction was always monoelectronic and reversible.

3. Results

3.1. Fluorescence and photoisomerization in the absence of quenchers

The data on the β -StN photoisomerization in the absence of quenchers are collected in Table 1. ϕ_i° and ϕ_c° are the fluorescence quantum yield of the *trans* isomer and the quantum yield of the direct *trans* \rightarrow *cis* photoisomerization respectively; α represents the fraction of β -StN triplets which decay to the ground state *cis* isomer and was obtained from the photostationary composition in the anthraquinone-sensitized isomerization according to the expression $[cis]/[trans] = \alpha/(1 - \alpha)$ for the triplet decay ratio for high energy triplet sensitizers [9]. In column 5 of Table 1 are given the values of the excited singlet \rightarrow triplet intersystem crossing quantum yield ϕ_{ISC} of *trans*- β -StN calculated from the relation $\phi_{ISC} = \phi_c^\circ/\alpha$, assuming a triplet mechanism for the direct *trans* \rightarrow *cis* photoisomerization.

3.2. Fluorescence quenching

The quenching of β -StN fluorescence by amines in non-polar media is accompanied by the appearance of a new fluorescence emission at longer wavelengths, which has been interpreted as being caused by the presence of exciplexes [6]. In the presence of electron acceptors the fluorescence of β -StN is quenched but, in acetonitrile as well as in methylene chloride, no changes in the shape of the fluorescence spectrum were observed. The Stern-Volmer coefficients K_{SV} (M^{-1}) for the quenching of the β -StN fluorescence are collected in Table 2 together with the polarographic reduction potentials E_a^{red} of the acceptors in acetonitrile. Since the reduction potential of the acceptor is linearly related to its ground state electron affinity, the observed

TABLE 1

Fluorescence and photoisomerization of β -StN in the absence of quenchers

Solvent	ϕ_i°	ϕ_c°	α	ϕ_{ISC}
Acetonitrile	0.51 ^a	0.18	0.50	0.36
Methylene chloride	0.40	0.14	0.55	0.25 ₅

^aData taken from ref. 6.

TABLE 2

Stern-Volmer coefficients for the quenching of β -StN fluorescence by electron acceptors

Quencher	Methylene chloride	Acetonitrile	E_a^{red} (V)
	K_{SV} (M^{-1})	K_{SV} (M^{-1})	
BN	—	—	−2.00
<i>p</i> -DCB	58	100	−1.14
TCTMC	94	119	−0.76
TCT	106	158	−0.17

increase of K_{SV} with decreasing E_a^{red} is indicative of a charge transfer from the excited singlet state donor to a ground state acceptor in the fluorescence quenching. The enhancement of K_{SV} in acetonitrile with respect to methylene chloride is also consistent with a charge transfer mechanism, even if the effect may be the result of a difference in the fluorescence lifetime of β -StN in the two solvents.

3.3. Effect of electron acceptors on the direct *trans* \rightarrow *cis* photoisomerization

The quantum yields ϕ_c of the direct *trans* \rightarrow *cis* photoisomerization of β -StN in acetonitrile and methylene chloride at various acceptor concentrations [Q] are given in Tables 3 and 4. The observed effects are similar in the

TABLE 3

Quantum yields ϕ_c of direct *trans* \rightarrow *cis* photoisomerization of β -StN at various acceptor concentrations in acetonitrile

[BN] (mM)	ϕ_c	[<i>p</i> -DCB] (mM)	ϕ_c	[TCTMC] (mM)	ϕ_c	[TCT] (mM)	ϕ_c
0	0.18	0	0.18	0	0.18	0	0.18
10.7	0.18	3.4	0.28	4.1	0.20	6.2	0.13
23.0	0.17	6.7	0.34	8.3	0.22	9.3	0.11
27.2	0.18	10.1	0.36	12.8	0.25	12.3	0.10
		15.2	0.40	16.8	0.26		
		27.0	0.44				

TABLE 4

Quantum yields ϕ_c of direct *trans* \rightarrow *cis* photoisomerization of β -StN at various acceptor concentrations in methylene chloride

[BN] (mM)	ϕ_c	[<i>p</i> -DCB] (mM)	ϕ_c	[TCTMC] (mM)	ϕ_c	[TCT] (mM)	ϕ_c
0	0.14	0	0.14	0	0.14	0	0.14
4.0	0.14	4.8	0.16	2.35	0.15	2.3	0.11
10.0	0.14 ₅	9.2	0.17	3.15	0.14 ₅	4.6	0.088
21.0	0.13 ₅	18.4	0.20 ₅	11.7	0.18	6.8	0.075
		23.4	0.21	19.6	0.19	9.1	0.069
		32.0	0.22			13.7	0.055

two solvents. In the presence of TCT, the strongest of the acceptors studied, ϕ_c decreases on increasing $[Q]$ whereas BN is without effect. With *p*-DCB there is a pronounced increase of ϕ_c as $[Q]$ increases. A slight increase of ϕ_c is observed also with TCTMC. It may be recalled that an enhancement in the photoisomerization quantum yield of β -StN has been found in non-polar solvents with diethylaniline as quencher [6].

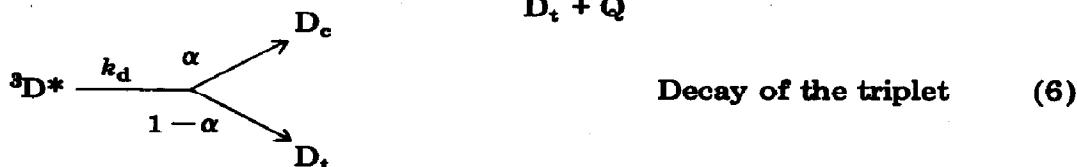
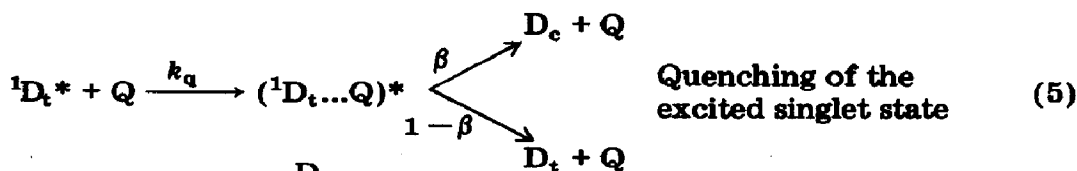
3.4. Photosensitized isomerization in the presence of electron acceptors

Within experimental uncertainty the photostationary states in the anthraquinone-photosensitized isomerization of β -StN are the same in the absence and in the presence of the electron acceptors ($[Q] < 3 \times 10^{-2}$ M). The latter also have no effect on the rates of the photosensitized *cis* \rightarrow *trans* and *trans* \rightarrow *cis* isomerizations, determined by starting from the pure *cis* and *trans* isomers. These results indicate that an interaction of the electron acceptors with the triplet state of β -StN is unlikely.

4. Discussion

The fluorescence of *trans*- β -StN is quenched by the electron acceptors, with the exception of BN, according to a simple Stern–Volmer law. The influence of the electron acceptor on the *trans* \rightarrow *cis* photoisomerization quantum yield ϕ_c is more complicated.

In a previous study [5] we have shown that the effect of azulene on the photoisomerization of β -StN is consistent with a triplet mechanism of the photoprocess. Therefore the following reaction scheme can be proposed for a discussion of the effect of electron acceptors on the fluorescence and photoisomerization yields of *trans*- β -StN:



where D_t and D_c are the *trans* and *cis* isomers respectively of β -StN, and Q represents the quencher (electron acceptor). The other symbols have their usual meanings. Application of the steady state treatment to the $^1D_t^*$ and $^3D^*$ species leads to the following expression for the direct *trans* \rightarrow *cis* photoisomerization quantum yield of β -StN:

$$\phi_c = \frac{\alpha k_{ISC} + \beta k_q [Q]}{k_t + k_{IC} + k_{ISC} + k_q [Q]} = \frac{\alpha \phi_{ISC} + \beta K_{SV} [Q]}{1 + K_{SV} [Q]} \quad (I)$$

where $\phi_{ISC} = k_{ISC}/(k_t + k_{IC} + k_{ISC})$ is the triplet yield in the absence of quenchers and $K_{SV} = k_q/(k_t + k_{IC} + k_{ISC})$ is the Stern–Volmer coefficient for the fluorescence quenching. Equation (I) can be rewritten in the form

$$\phi_c = \frac{\alpha \phi_{ISC} - \beta}{1 + K_{SV} [Q]} + \beta \quad (II)$$

Plots of ϕ_c versus $(1 + K_{SV} [Q])^{-1}$ are given in Fig. 1. Despite the experimental uncertainty in the quantum yield measurements, the agreement with eqn. (II) is satisfactory. The intercepts of these plots at $(1 + K_{SV} [Q])^{-1} = 0$ give the *cis*-isomer yields β in the quenching process and these are shown in Table 5 for the various electron acceptors.

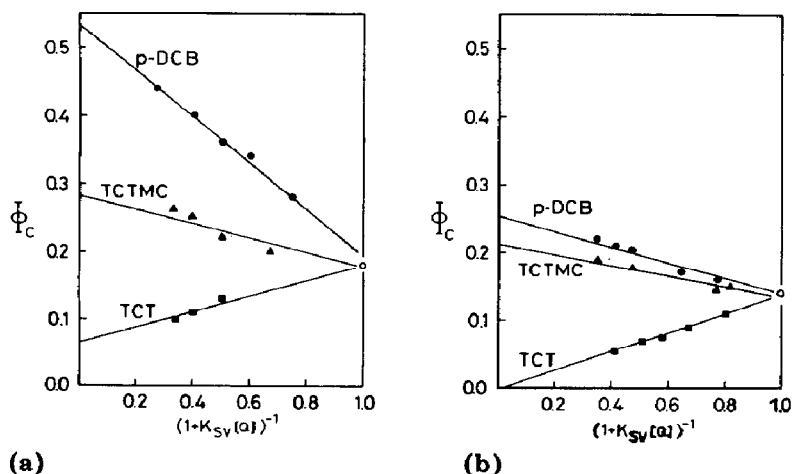


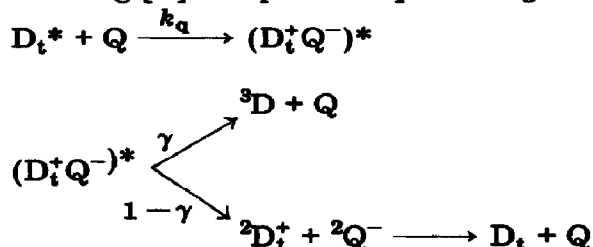
Fig. 1. Plots of ϕ_c vs. $(1 + K_{SV} [Q])^{-1}$ according to eqn. (II) for β -StN in (a) acetonitrile and (b) methylene chloride.

TABLE 5

Isomerization yields β in the quenching of β -StN fluorescence by various electron acceptors

Quencher	Isomerization yield β	
	Methylene chloride	Acetonitrile
<i>p</i> -DCB	0.25	0.53
TCTMC	0.21	0.28
TCT	0.00	0.07

With the exception of BN, in both solvents a decrease in the β values is observed as the quenching efficiency of the acceptor increases. If a triplet mechanism for β -StN isomerization is still operative in the presence of the acceptors, the observed effects may be related to the influence of the exciplexes on the intersystem crossing yield in the donor molecule. In this case the following [7] is a possible quenching mechanism:



Here an initially formed exciplex $(D_t^+ Q^-)^*$ is either converted to an ion pair (or to free ions) or gives the triplet 3D , the relative efficiencies of the two processes being dependent on the strength of the donor-acceptor charge transfer interaction.

According to this scheme $\gamma = \beta/\alpha$, where α is the triplet decay ratio. With *p*-DCB in acetonitrile we should have $\gamma \approx 1$, whereas in the presence of TCT a quenching of the ${}^1D_t^*$ state without intersystem crossing should be the predominant path, especially in methylene chloride.

The intermediacy of radical ions in the isomerization, which has been ruled out for stilbene exciplexes [7], cannot be definitely excluded in our case. As shown in Table 5 the β values are larger in acetonitrile where a greater stabilization of the radical ions is expected. However, the marked decrease in the isomerization yield with decreasing acceptor reduction potential is evidence against the participation of radical ions. Further investigations, in particular the detection of transient intermediates by pulsed photolysis measurements, are needed for a more detailed discussion of the quenching mechanism.

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