A LASER FLASH PHOTOLYSIS STUDY OF THE TRIPLET STATE OF *trans*-AZASTILBENES

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Summary

Information on the triplet state of *trans*-mono-azastilbenes (*n*-styrylpyridines) (*n* is an integer) and *trans*-diazastilbenes (*n,n'*-dipyridylethylenes) has been obtained from a laser flash photolysis study. Transient spectra in the ranges 320 - 400 nm and 50 - 90 ns, which can be ascribed to the T–T absorption of azastilbenes, were observed at room temperature in the presence of xanthone as a high energy triplet donor and at low temperatures by direct excitation. The triplet yield measured in a rigid matrix at 77 K was found to be markedly lower for the meta *N*-positional isomers. The mechanism of deactivation of the electronically excited *trans*-azastilbenes, hypothesized on the basis of fluorometric, photochemical and theoretical studies, was confirmed.

1. Introduction

As in the case of stilbene [1], both singlet and triplet excited states of azastilbenes are reactive in the trans → cis photoisomerization, as demonstrated from sensitized experiments on styrylpyridines (*n*-StPs) (*n* is an integer) and dipyridylethylenes (*n,n'*-DPEs) [2 - 4]. An experimental study of the effect of temperature on the photophysical properties of *trans-n*-StPs has indicated that the activated twisting around the central double bond, which is dominant at room temperature, takes place in the singlet manifold [5, 6], as for stilbene [1]. Only at low temperatures, when the rotation is inhibited, can the $S_1 \rightarrow T_1$ intersystem crossing (ISC) become important, at least for some *N*-positional isomers.

A theoretical study [7] of the lowest excited states of StPs and DPEs, based on INDO/S calculations, has shown that the S_1 and T_1 states have a π,π^* stilbene-like character. The determination of the spin–orbit coupling, based on the interaction between $^{1,3}\pi,\pi^*$ and $^{3,1}n,\pi^*$ states, has led to the derivation of relatively high rate constants of ISC for 2-StP and 4-StP (1.6×10^9 s^{-1} and 4×10^9 s^{-1} respectively) and a much lower value for

3-StP (4×10^7 s^{-1}), owing to the nodal properties of the π and π^* molecular orbitals in the meta position of the ring [5 - 9]. Similar results were obtained for the symmetrical 2,2'-, 3,3'- and 4,4'-DPEs [7]. These theoretical predictions are in good agreement with the experimental results on the photophysical and photochemical properties of StPs [5, 6], showing that the activated twisting in the singlet manifold from the trans (^{1}trans) to the perpendicular configuration (^{1}perp), from which internal conversion to the ^{0}perp ground state and partitioning to the trans and cis forms takes place, is the main deactivation pathway of S$_1$. In fact, the rate parameter k_{tp} for twisting is always much larger than both the fluorescence and the ISC rate parameters, k_F and k_{ISC}, for all isomers at ambient temperature. At low temperatures, when k_{tp} is drastically reduced, the competition of ISC with fluorescence becomes important and a substantial fraction of molecules can deactivate through the triplet manifold, at least for the ortho and para N-positional isomers [5 - 7].

It would be interesting to obtain conclusive direct proof for this interpretation of the deactivation mechanism of azastilbenes by a flash photolysis study of their T$_1$ $\rightarrow$ T$_n$ absorption. There was no direct information on the triplet states of these compounds. A previous attempt to detect triplet transients by laser flash photolysis at room temperature gave negative results [10]. The present study indicates that T–T absorption of azastilbenes can be readily observed in very viscous media or in fluid solutions by sensitization experiments, but triplet transients are generally undetectable by direct excitation at ambient temperature.

2. Experimental details

trans-n-StPs (n = 2, 3, 4) and 3,3'-DPE had been synthesized for previous work [6, 11]; the standard procedure is described elsewhere. 2,2'- and 4,4'-DPE were commercial products from Raschig G.m.b.H. and were recrystallized before use. 2-Methyltetrahydrofuran (2-MTHF) from Aldrich-Chemie or Merck, Darmstadt, was distilled before use by standard procedures (and was kept free of peroxides, which is important for λ_{exc} < 300 nm). The samples were purged with argon.

The corrected fluorescence spectra were recorded with a Perkin–Elmer MPF-44 spectrofluorometer and an Oxford Instruments cooling unit with a CF-204 continuous-flow cryostat. For determination of the quantum yields of DPEs in 3-methylpentane (3-MP) at 77 K (three independent experiments; mean deviation, about 5%), the standard used was 9,10-diphenylanthracene under the same conditions (ϕ_F = 1). For more details, see ref. 6.

Flash photolysis measurements were carried out with two laser systems, the 248 nm pulse of an excimer laser (Lambda Physik, EMG 200) and the third and fourth harmonics of a neodymium laser (J. K. Lasers, type 2000). The former was applied most frequently. The excitation wavelengths 265 nm

and 353 nm were only used for glycerol triacetate and for sensitized excitation respectively. The set-up and method of data acquisition have been described elsewhere [12]. The transients of the olefin acceptors were measured at relatively high concentrations (0.01 M or above), this being necessary to reduce the lifetime of the triplet donor (xanthone) to about 10 ns. Moreover, the olefin fluorescence interferes with the absorption measurements (*cf.* ref. 12). Therefore it was not possible to achieve good spectral separation of the distinct T–T absorption spectra in the presence of the sensitizer, and the triplet lifetimes reported in Table 1 have a larger error than usual (about 20%).

TABLE 1

Fluorescence quantum yields of azastilbenes in inert solvents at room temperature [2, 6], derived parameters estimated by calculation [7] and triplet lifetimes in acetonitrile (data for stilbene are reported for comparison)

Compound	$\phi_F{}^a$	τ_F^{calc} (ps)	ϕ_{ISC}^{calc}	τ_T (ns)
Stilbene	0.036	90	0.004	60
2-StP	0.0008	3	0.005	70
3-StP	0.075	221	0.009	60
4-StP	0.0016	4	0.016	50
2,2'-DPE	0.005	16	0.016	90
3,3'-DPE	0.13	394	0.098	60
4,4'-DPE	0.0004	0.8	0.004	70

[a]From ref. 6 (for StPs in *n*-hexane) and ref. 2 (for DPEs in benzene).

Both fluorescence and flash photolysis data in 2-MTHF have to be considered with caution since it is probable that aggregation phenomena [13] will influence the results at liquid nitrogen temperature with the concentrations used (about 5×10^{-5} M for ϕ_F determination and $(2 - 10) \times 10^{-4}$ M for measurement of T–T absorption). Moreover, they were not corrected for the changes in the ground state absorbance with temperature at λ_{exc}.

3. Results and discussion

Figure 1 shows the transients observed on direct excitation of the six compounds investigated in 2-MTHF at 77 K. They are assigned to the lowest trans triplet state by comparison with the transients formed by energy transfer from a high energy triplet donor and were clearly observable when the sensitizer triplet was fully quenched. It is noteworthy that no structure could be detected in the T–T absorption spectrum in contrast to the case of *trans*-stilbene.

At room temperature the transient optical density ΔOD, which is a measure of the triplet yield, of StPs and DPEs is very low, as for stilbene [1], so that the transients were detectable only in the presence of sensitizers. Xanthone in acetonitrile ($\lambda_{exc} = 353$ nm) was used throughout (other
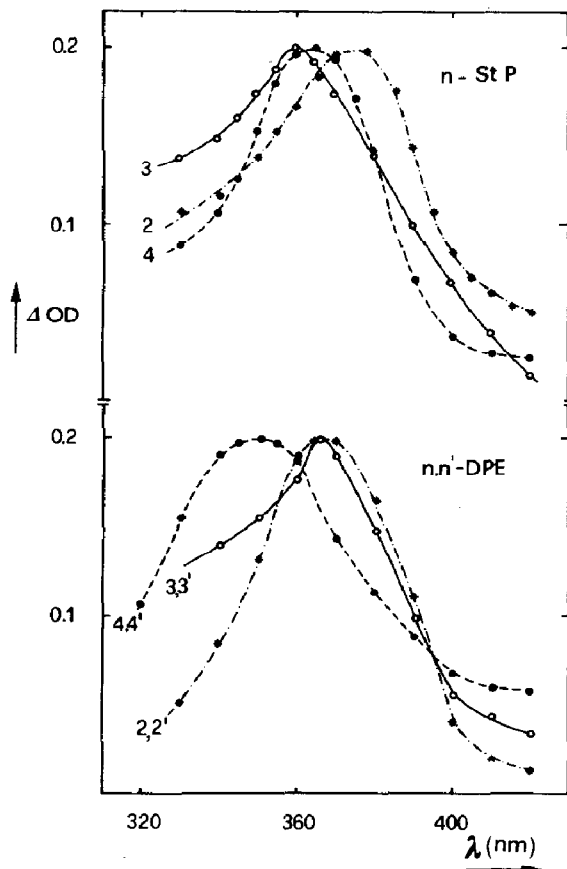
Fig. 1. Normalized triplet–triplet absorption spectra of trans StPs and DPEs in 2-MTHF at 77 K (λ_{exc} = 248 nm).

sensitizers, *e.g.* benzophenone, were less suitable). The T–T absorption spectra of the olefin acceptors display their maximum around 360 nm; their lifetime τ_T is shorter than 100 ns (see Table 1, last column). Only for DPEs in various solvents was a weak transient at 360 nm still observable at room temperature without the sensitizer. In addition to this, a long-lived stronger absorption around 450 nm was observed on direct excitation of DPEs. Further work is in progress to assign this transient, which could be due to hydrogen abstraction from the solvent [9, 14].

The triplet yield and the lifetime increase on increasing the solvent viscosity and/or decreasing the temperature. A plot of log τ_T^{-1} *vs.* T^{-1} has two distinct sections, as shown in Fig. 2 for 2-StP in glycerol triacetate and 2-MTHF. By analogy with previous studies on similar olefins [12, 15], two temperature regions can be distinguished, below and above a certain critical temperature (about 230 K and about 150 K for glycerol triacetate and 2-MTHF respectively). The behaviour is determined by the viscosity of the medium. In the higher temperature region it appears that a ^{3}trans $\rightleftharpoons$ ^{3}perp triplet equilibrium is established. The linear dependence of log τ_T^{-1} on T^{-1} below this characteristic temperature reflects the hindrance, caused by the
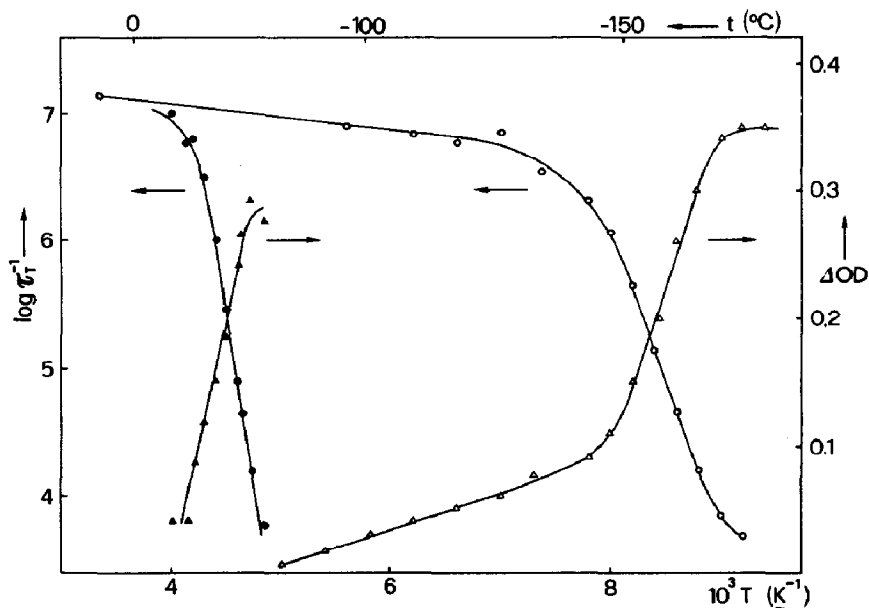
Fig. 2. Optical density from triplet absorption at 370 nm (triangles) and reciprocal life-time (circles) *vs.* T^{-1} in glycerol triacetate (full symbols) and 2-MTHF (open symbols) for trans 2-StP.

increasing viscosity, to the twisting around the central double bond towards the perp configuration. At even lower temperatures, the triplet lifetime approaches a constant value (*e.g.* 10 ms or longer in 2-MTHF), reflecting the direct decay to ^{0}trans without twisting. Under such conditions, no isomerization occurs and the radiationless physical deactivations, namely the ^{1}trans → ^{0}trans internal conversion and the ^{1}trans → ^{3}trans ISC (followed by ^{3}trans → ^{0}trans), remain the only processes competing with fluorescence.

Figure 2 also shows the corresponding increase in ΔOD for 2-StP which reflects the increase in the triplet yield on decreasing the temperature. In 2-MTHF both the change in temperature and the viscosity seem to be responsible for the increase in ΔOD on cooling. The limiting values measured in a rigid matrix were used to estimate the relative triplet quantum yields ϕ_T^{rel} reported in Table 2. Similar dependences of ΔOD and τ_T on temperature were also observed for 2,2'- and 4,4'-DPE in several media but were not systematically investigated. In 2-MTHF, slightly above 77 K, $\tau_T \geqslant 10$ ms was measured in each case. The second transient around 450 nm observed on direct excitation of DPEs at ambient temperature disappeared at high viscosity.

Rough estimation of the fluorescence lifetime τ_F (from the experimental ϕ_F in fluid inert solvents at room temperature [2, 6] and the natural lifetimes which had been evaluated, by comparison with stilbene, from the oscillator strengths and electronic transition energies calculated by the INDO/S method [7]) indicated values of a few picoseconds for the ortho and para isomers and higher values (by one to two orders of magnitude) for

TABLE 2

Comparison between the absolute and relative fluorescence quantum yields and the relative triplet yields of azastilbenes at 77 K

Compound	$\phi_{\mathrm{F}}^{\mathrm{a}}$ (in 3-MP)	$\phi_{\mathrm{F}}^{\mathrm{rel}}$ (in 2-MTHF)	$\phi_{\mathrm{T}}^{\mathrm{rel}}$
2-StP	0.42	0.48	0.45
3-StP	1.00	0.82	0.12
4-StP	0.20	0.38	0.20
2,2'-DPE	0.13	0.11	1.00
3,3'-DPE	0.60	1.00	0.25
4,4'-DPE	0.07	0.02	0.35

[a]Values for StPs are taken from ref. 5; values for DPEs are from ref. 16.

the meta isomers. From these fluorescence lifetimes, reported in Table 1, and the approximate ISC rate parameters calculated [7], one obtains the rather small ϕ_{ISC} given in the fourth column of Table 1. This confirms that practically all decay of azastilbenes from ¹trans at room temperature occurs in the singlet manifold by fast internal rotation to the perp configuration and possibly by "vertical" internal conversion to ⁰trans. Both ϕ_{F} and ϕ_{ISC} are expected to increase markedly at low temperature when the ¹trans → ¹perp rotation is inhibited. Table 2 shows the ϕ_{F} values measured in 3-MP at 77 K together with the relative fluorescence and triplet yields in 2-MTHF at the same temperature. The relative yields, $\phi_{\mathrm{F}}^{\mathrm{rel}}$ and $\phi_{\mathrm{T}}^{\mathrm{rel}}$, were normalized to those of the compounds which display the maximum yield of fluorescence (3,3'-DPE) and triplet formation (2,2'-DPE) respectively.

When compared with the $\phi_{\mathrm{F}}^{\mathrm{rel}}$ obtained in the same medium, the $\phi_{\mathrm{T}}^{\mathrm{rel}}$ of the azastilbenes at 77 K show a trend which is in qualitative agreement with what would be expected on the basis of competition between fluorescence and ISC. In fact, the azastilbenes with the heteroatom in the meta position, characterized by the highest ϕ_{F}, have the lowest ϕ_{ISC} whilst the ortho and para aza-analogues show the opposite behaviour. This complementarity no longer exists when the ortho and para isomers themselves are compared. However, this might be expected from the limited reliability of the data (see Section 2) and from the probable involvement of ¹trans → ⁰trans internal conversion for these particular isomers, probably resulting from strong mixing between the lowest excited singlet state of ethylenic character with the n,π^* state located nearby. The contribution of this decay channel to the overall decay of ¹trans had already been hypothesized to explain the relatively lower quantum yield ϕ_{C} of trans → cis photoisomerization of 2- and 4-StP in non-polar solvents at room temperature [6]. Internal conversion seemed to become negligible in polar solvents since ϕ_{C} increases in acetonitrile up to the maximum value of about 0.5 and ϕ_{F} reaches a value close to unity in EPA at 77 K [5, 6, 17].

4. Conclusions

The present findings constitute the first results on the triplet behaviour of azastilbenes and confirm the validity of hypotheses derived from the study of the fluorescence and the photoreaction mechanism. In particular they confirm the importance of the deactivation of ^{1}trans through the triplet manifold at low temperature when the heteroatom is ortho or para to the styryl group [5, 7]. Finally, they provide evidence that internal conversion competes with ISC for these isomers [5, 6].

Acknowledgments

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