

PHOTOPHYSICAL AND PHOTOCHEMICAL BEHAVIOUR OF STILBENE-LIKE
MOLECULES AND THEIR AZA-ANALOGUES

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Abstract - The main photoreactions (isomerization and cyclization) and luminescence of stilbene analogues where polynuclear aryl groups or pyridyl groups are joined through an ethylene bridge have been investigated. More details are given about two series of compounds, the styrylnaphthalenes and the styrylpyridines. The naphthyl analogues of stilbene may have a lowest excited state of a naphthalene character which induces a reduction of the radiative rate parameters, possibly opening a triplet path to isomerization. The low-lying n, π^* states of the azastilbenes contribute to open non-radiative paths for the decay from S_1 , especially for ortho and para aza-compounds. Internal conversion is important in fluid media whilst intersystem crossing may be operative in a rigid matrix at low temperatures. Bimolecular processes of the excited diarylethylenes and their aza-analogues with suitable additives (energy, proton and electron donors or acceptors) are also described. It is shown how they can selectively populate the singlet or triplet manifolds of the olefins. Finally, conformational equilibria involving rotation of the aromatic groups about the quasi-single bonds are described. A fluorimetric analysis of the mixture of the two conformers postulated allows the photophysical parameters of the single components to be evaluated.

INTRODUCTION

This paper deals with the photophysical and photochemical behaviour of flexible stilbene-like molecules and their aza-analogues, a subject which has been under study for a long time in our laboratory. The behaviour of trans stilbene (St) has been extensively studied and the photoreaction mechanism has been satisfactorily elucidated (Refs. 1-3). Excitation of S_1 (B_u^* state) is assumed to be followed by internal rotation about the central double bond leading to internal conversion (IC) $S_1 \rightarrow S_2$ via a potential energy barrier located near the avoided potential crossing of S_1 and S_2 (probably a doubly excited state, A_g^{**}) (Refs. 2,4). The successive IC $S_2 \rightarrow S_0$ is assumed to take place in the perpendicular configuration (perp) where the energy gap is smallest, thus giving rise to isomerization (see Fig. 1). The twisted configuration is also thought to be reached by irradiation of cis St, which can isomerize reversibly. It is to be recalled that St, like other diarylethylenes, can undergo other photoreactions besides isomerization, as schematized here:



The fluorescent $^1_{trans}*$ can give dimerization to tetraphenylcyclobutane in concentrated solutions ($>10^{-3}M$) (Ref. 5) and reduction to ethane-derivatives or solvent addition (observed for some aza-derivatives in hydrogen donating sol-

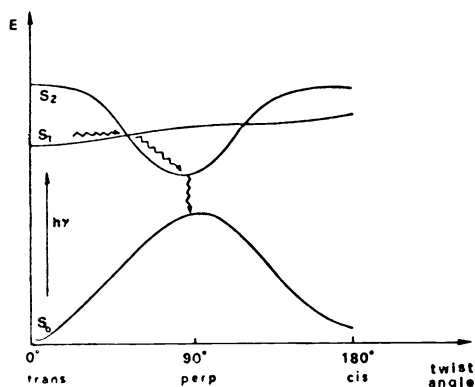


Fig. 1. Potential energy diagram for the lowest singlet states of stilbene as a function of the ethylene bond rotation (see Ref. 2).

vents)(Ref. 6). The $^1\text{cis}^*$ isomer, which is generally non-fluorescent at room temperature, can cyclize to dihydrophenanthrene (DHP), which may then be oxidized to phenanthrene by hydrogen acceptors. Triplet states, populated by sensitizers, undergo only cis-trans isomerization.

The main object of the present study is to investigate the role of two structural factors, namely the replacement of one or both of the phenyl groups of St with: i) aromatic polycyclic groups (naphthyl, phenanthryl, etc.).

In such cases, steric and electronic factors may affect the ordering of the excited states and the shape of the potential energy surfaces. The rate of the competing deactivation processes can consequently change with the structure of the various compounds.

- ii) heteroaromatic groups (pyridyl, quinolyl, etc.). The n, π^* states introduced by the heteroatom affect the behaviour of the corresponding compounds to an extent which depends on the nitrogen atom position. The main effect of the proximity of these n, π^* states to the lowest π, π^* states is to open new non-radiative paths to the deactivation of the excited molecules, thus modifying their photoreactivity.

Recent and new results obtained in our laboratory, supplemented with some literature data, will be discussed, taking St as a model compound, in order to elucidate the structural factors which control the behaviour of excited diarylethylenes. Asymmetrically substituted ethylenes $\text{Ar}_1\text{-CH=CH-Ar}_2$ (Ar_1 = phenyl, Ar_2 = polycyclic or pyridyl group) were investigated in a greater detail. Among them, styrylnaphthalenes (StN's) represent typical examples of St analogues having condensed-ring side groups; styrylpyridines (StP's) are typical examples of aza-stilbenes. Greater attention will be dedicated to these two series of compounds.

Bimolecular processes, occurring during the lifetime of these excited molecules with suitable additives such as energy, proton and electron donors (or acceptors), will be reported to show how such additives enable one or another of the competing deactivation processes to be preferred.

Since luminescence and photoreactions of stilbene-like molecules are generally dependent on the excitation energy because of the presence in solution of rotational conformers involving the quasi-single bonds, a fluorimetric study of the conformational equilibria will also be reported.

TRANS DIARYLETHYLENES CONTAINING POLYCYCLIC GROUPS

Replacement of a phenyl group of St with larger condensed-ring groups (naphthyl, phenanthryl, etc.) which causes a loss of the two-fold symmetry characterizing St, may have two main perturbative effects: i) steric interaction between the

aryl groups and the ethylenic hydrogens; ii) changes in the nature of the lowest excited state. The first effect can be important in determining the composition of the mixtures of conformers (see below). As a consequence of the second effect, the first electronic transition can be partially localized in the aryl group thus changing the properties of the excited molecule (fluorescence, photoreactivity, etc.)(Ref. 7).

Non-bonded interactions between the aryl groups and the trans ethylene hydrogens are small in St, as well as when Ar₁ and/or Ar₂ are, e.g., 2-naphthyl, 2- and 3-phenanthryl, 2-anthryl. All these molecules can achieve a high degree of coplanarity among the three chromophores. The interactions are larger when the aryl groups are, e.g., 1-naphthyl, 1- and 9-phenanthryl, 1-anthryl and 3-pyr-enyl. In these cases, there is a hypochromic and hypsochromic effect on the absorption spectrum and a change in the shape of the band (loss of vibrational structure and/or broadening of the band)(Ref. 8). For these two series of compounds, as found for St (Ref. 1), the decay of ¹trans* can be accounted for by either fluorescence or photoreaction in the singlet or triplet manifold. The main effect of polycyclic side groups is to alter the ratio between the reactive and radiative decay paths, the latter becoming an important process in an inert rigid matrix at liquid nitrogen temperature. The larger steric interactions in 9-anthryl and 4-phenanthryl derivatives favour radiationless transitions in these compounds and their behaviour is expected to be quite peculiar. As to the ordering of the lowest excited states, simple considerations based on the energy, oscillator strength and orientation of the transition moment for the lowest electronic transitions of styrene and the aromatic groups (naphthalene, phenanthrene, etc.), point out that excitation to the lowest excited singlet state is probably localized in the aromatic group for 2-StN (at least for one of its conformers, see below) as well as for some larger analogues. Strong steric interactions (deviation from planarity) and a lowest excited state of an aromatic nature can noticeably affect the rate of isomerization of the trans compounds and of both isomerization and cyclization of the cis compounds.

Styrylnaphthalenes

Molecular orbital calculations in the PPP approximation have indicated that the lowest excited state is "naphthalenic" in character for trans 2-StN and "stilbenic" for 1-StN (Ref. 8). This was confirmed by the absorption spectrum of 2-StN obtained in a rigid matrix at low temperature (Fig. 2) which shows a weak

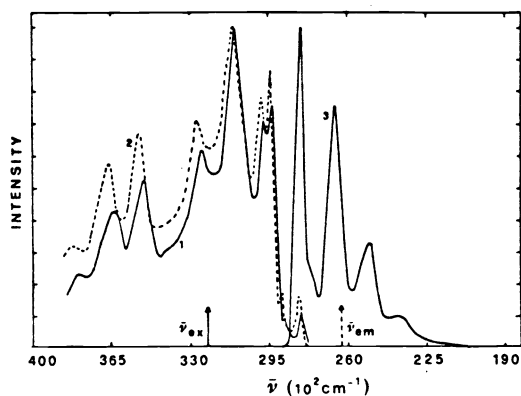


Fig. 2. Absorption (1), excitation (2) and fluorescence (3) spectra of 2-StN in 3-methylpentane at 77 K.

band ($S_0 \rightarrow S_1$), with a naphthalenic vibrational frequency, on the red tail of the stronger band ($S_0 \rightarrow S_2$), the latter being assigned to a delocalized transition (conjugation band)(Ref. 8). No sign of such a band was observable in the corresponding 1-StN where it is probably hidden under the red-shifted stilbenic band. The fluorescence spectrum of 2-StN corresponds to the weak band and is naphthalene-like. The consequence of the naphthyl substitution is a high fluorescence yield and a relatively low photoisomerization yield at room temperature (see Table 1), probably because of an activated internal rotation in S_1 that is slower than for St. In addition, 2-StN has a much longer average lifetime, almost an order of magnitude larger than 1-StN. The difference in life-

TABLE 1. Fluorescence (ϕ_F) and trans \rightarrow cis photoisomerization (ϕ_C) quantum yields in two solvents, lifetimes (τ_F , ns) and kinetic parameters of radiative and non-radiative decay (k_F and k_{nr} , 10^8 s^{-1}) in n-hexane at room temperature ($\lambda_{ex} = 315 \text{ nm}$) for some trans styrylnaphthalenes, styrylphenanthrenes (StPh's) and for 9-styrylanthracene (9-StA), compared to stilbene.

Compounds	n-hexane					acetonitrile	
	ϕ_F	ϕ_C	τ_F	k_F	k_{nr}	ϕ_F	ϕ_C
St	0.036	0.43	0.09 ^c	4.0	108	0.016	0.45
1-StN ^a	0.64	0.14	1.9	3.4	1.9	0.25	0.28
2-StN ^b	0.83	0.12	5.1	1.6	0.3	0.51	0.18
	0.50		27.6	0.2	0.2		
1-StPh	0.54	0.25	9.8	0.6	0.5		
2-StPh	0.25		30.5	0.1	0.3		
9-StPh	0.60	0.16	5.3	1.1	0.8	0.13	0.35
9-StA	0.30		3.7	0.8	1.9		

Note a. From Ref. 9. Note b. The two parameters reported for 2-StN refer to different rotamers and are derived from the fluorimetric analysis of the conformer mixture. Note c. From Ref. 10.

time between the 1 and 2 isomers is due to larger radiative and non-radiative decay rate parameters for 1-StN. In fact, the latter has the same value of k_F as St (but a very smaller k_{nr}), while 2-StN has k_F values that are intermediate between those of St and naphthalene ($k_F \sim 2 \times 10^6 \text{ s}^{-1}$, see Ref. 11) and are particularly low for the longer-lived conformer. The k_{nr} values of 2-StN are also much smaller than St and 1-StN, which could reflect either a higher barrier to rotation in S_1 or even a spin forbidden process. There is a marked decrease in ϕ_F on going from a non-polar to a polar solvent. This may appear unusual for aromatic hydrocarbons (Ref. 11), but a similar effect is known for St itself (Ref. 12) and for higher diphenylpolyenes (Ref. 13). The ϕ_F of St and its decrease in polar solvents is, however, too small to lead to an observable parallel increase of ϕ_C which is already high (near to 45-50%) at room temperature. The stronger polarity effect observed with StN's leads to a marked decrease in ϕ_F and a coupled enhancement in ϕ_C . The effect might be due to a specific (e.g., charge transfer) interaction of the olefin with the polar solvent leading to isomerization via enhanced intersystem crossing (ISC). An alternative explanation can be based on a solvent effect on the potential energy curves as a function of the rotation angle about the double bond. The B_u^* state (more polarizable, particularly for asymmetric diarylethylenes) is expected to be more sensitive to solvent changes than is the A_g^{**} state (of partially covalent character). Acetonitrile thus might stabilize the B_u^* state (compared to n-hexane) resulting in an increase in the angle at which the avoided crossing occurs and in a decrease of the potential barrier to rotation (Ref. 12). It should be recalled that the strong solvent dependence of ϕ_F and τ_F for diphenylpolyenes has been attributed to changes in the energy gap between the B_u^* and A_g^{**} states due to solvent polarity (Ref. 13). The different nature of the S_1 state of 2-StN could lead to an increase of the triplet yield compared to St. For the latter, the $S_1 \rightarrow T_1$ ISC is a minor process and no triplet transients were observed by flash photolysis at room temperature (Ref. 1). In fact, T-T absorption has been observed by laser flash photolysis of 2-StN at room temperature (Ref. 14 and present work). The yield, however, has not been measured, but there is an indication, confirmed by azulene quenching experiments, that it is probably low even in this case (Refs. 14b,15).

A study of the temperature effect, which proved to be valuable for interpreting the photoreaction mechanism of St (Ref. 1) was also undertaken for StN's. The

fluorescence quantum yield was measured as a function of temperature and analyzed by means of eq. 1 (where IC is considered to be negligible and only the

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + A_F e^{-\Delta E_F/RT}} \quad (1)$$

internal rotation about the central double bond is considered to be an activated process) and eq. 2

$$\ln\left(\frac{\phi_F^{\text{lim}}}{\phi_F} - 1\right) = \ln \frac{A_F}{k_F + k_{ISC}} - \frac{\Delta E_F}{RT} \quad (2)$$

where $\phi_F^{\text{lim}} = k_F/(k_F + k_{ISC})$ is the fluorescence yield measured in a rigid matrix at 77 K when the activated process is inhibited. The Arrhenius parameters thus calculated show that the behaviour of naphthyl compounds is quite different from St, not only in the case of the 2 isomer, which has a S_1 state of naphthalenic character, but also in the case of the 1 isomer, where the S_1 state of a prevalently stilbenic character is probably mixed with a S_2 naphthalenic state located nearby. In fact, the energy barrier measured from fluorescence of StN's in 3-methylpentane (3-MP) is practically negligible below room temperature (150-290 K) whilst it becomes important (~ 7 kcal mol⁻¹) above room temperature (290-350 K). This is in qualitative agreement with what was found by E.Fischer et al. (see Fig. 2 in Ref. 16). Interestingly, these authors measured the energy barrier for the trans \rightarrow cis photoreaction (see Table 2)

TABLE 2. Quantum yields of photoreactions and activation energies of the trans \rightarrow cis photoisomerization for stilbene and its naphthyl analogues in methylcyclohexane:2-methylpentane 2:1 extrapolated from curves of ϕ vs. temperature in Ref. 16.^a

Compound	ϕ_C	ΔE_C (kcal mol ⁻¹)	ϕ_T	ϕ_{DHP}
St	0.50	3.5	0.32	0.1
1-StN	0.15	3.5	0.04	0.28
1,1'-DNE	0.08	4.0	0.04	0.2
2-StN	0.18	1.5	0.30	0.13
2,2'-DNE	0.08	2.5	0.30	(0.1)

Note a. ϕ_T and ϕ_{DHP} represent the quantum yields for cis \rightarrow trans isomerization and cyclization to dihydrophenanthrene, respectively.

and found a ΔE_C of 1.5 kcal mol⁻¹ for 2-StN and a sensibly higher one of 3.5 kcal mol⁻¹ for 1-StN. A similar behaviour was reported for the di-naphthyl-derivatives (DNE's). However, the absence of a barrier from fluorescence measurements means that the activated process does not compete with fluorescence in the low temperature range, probably because the internal rotation in S_1 has a negligible rate in comparison with k_F .

An intervention of a mixed mechanism seems to be the most plausible explanation of the experimental facts. A predominant triplet mechanism could be operative at room (see also Ref. 17) and lower temperatures, particularly for the longer-lived conformer of 2-StN whose ϕ_F is sensibly low (0.5) even at 77 K. The situation changes above room temperature. Here, ϕ_F and ϕ_C are coupled, as in the case of St (Ref. 1), probably because at these temperatures the internal rotation in S_1 becomes competitive with fluorescence. Therefore, a singlet mechanism can become prevalent above room temperature.

Styrylphenanthrenes

Energetic considerations ($E_{S_1} \sim 29,000 \text{ cm}^{-1}$ for phenanthrene) would suggest that in the case of phenanthryl derivatives, too, the excitation to S_1 could be localized in the aromatic group. Preliminary results are shown in Table 1. They indicate that 2-StPh resembles more 2-StN while 9-StPh displays a behaviour more similar to 1-StN and 1-StPh has an intermediate behaviour. The 9 compound was studied in a greater detail (see Table 1). Even in this case, ϕ_F is independent of temperature in the range 77-300 K in 3-MP ($\phi_F = 0.6$ at 77 K), and a triplet mechanism could be hypothesized. The lifetime is probably an average value (best fit of the apparently mono-exponential decay) for the two conformers, one of which should predominate in solution on the basis of steric interactions. The parameters reported show that the behaviour is similar to that of StN's (see Table 1), particularly of 1-StN and the shorter-lived conformer of 2-StN. The solvent effect is even larger in the case of 9-StPh. In ethanol, a ΔE_F of about 6 kcal mol^{-1} was found, which probably indicates a reduction of the energy barrier in S_1 and the opening of the singlet mechanism in polar solvents.

Pyrenyl-derivatives

Interesting results have been reported for 3-styrylpyrene (3-StPyr) and 1-naphthyl,3-pyrenyl-ethylene (1,3-NPyrE) (Ref. 18). The main decay of $^1\text{trans}^*$ is by fluorescence which has a practically unitary yield even at room temperature. Only in air-saturated solutions does it decrease to 0.7. The photoreaction quantum yield of 3-StPyr is very low, the sum of both isomerization and dimerization to tetra-arylcyclobutane being only 0.04. Surprisingly, dimerization, which normally takes place in concentrated solutions ($>10^{-3}\text{M}$) has been detected here over a wide concentration range (10^{-5} - 10^{-2}M). On the other hand, the cis compound has a high isomerization yield ($\phi_T = 0.7$) and cyclizes only in the presence of iodine as an oxidant (see below). Similar behaviour has been reported for 1,3-NPyrE but no interpretation has been given (Ref. 18).

Anthryl-derivatives

When the aryl groups are large (e.g., anthryl groups) neither one of the two geometrical isomers can be coplanar with the central double bond, steric hindrance being relieved by twisting about the quasi-single bonds. The study of 9-styrylanthracene (9-StA) has just begun in our laboratory. Only data on its luminescence are available at the present; these are shown in Table 1. Dianthrylethylenes (DAE's) have recently been described by H D. Becker et al. (19). The molecular geometries of cis compound (anthryl groups perpendicular to the plane of the ethylenic bond) and trans compound (anthryl groups twisted by about 50° about the quasi-single bonds and aligned parallel to each other) have been suggested to be responsible for their low photoreactivity ($\phi_C \sim 0$, $\phi_T \sim 0.0007$ and a very low yield of intramolecular [4+4] cycloaddition of cis isomer) and their very low fluorescence yields at room temperature. Radiationless decay to the ground state has been tentatively conceived to take place through a biradical species obtained by C-9 and C-9' bond formation.

TRANS DIARYLETHYLENES CONTAINING HETEROATOMS

Styrylpyridines

A systematic study was carried out on the properties of StP's in order to determine the effect of the introduction of n, π^* states by comparing them with St. The results of INDO/S (Ref. 20) and CNDO/S (Refs. 21,22) calculations, in agreement with the spectral behaviour, indicate that the lowest excited singlet state of StP's is "stilbenic" in character, the n, π^* states being almost 0.5 eV above it. The n, π^* excitation is prevalently confined to the pyridine ring for the 3 isomer while in the 2 and 4 isomers it involves a charge transfer from the pyridine to the benzene ring. Table 3 shows the quantum yields of fluorescence, photoisomerization and non-radiative deactivation (ϕ_{nr}) of trans StP's and St. The short lifetimes of StP's, estimated by comparison with St, as will be described below, and the rate parameters for radiative decay (k_F) are also reported. The ϕ_C values can be compared with ϕ_{nr} values if one takes into account that only a fraction (~ 0.5) of the twisting molecules which reach the perp configuration go to the cis ground state. Consequently, only the 4 isomer and particularly the 2 isomer have a substantial fraction of non-radiative decay which does not lead to isomerization. In fact, when the nitrogen atom is in a meta position (3-StP) the fluorescence and photoisomerization quantum

TABLE 3. Photophysical and photochemical parameters of trans styrylpyridines (Ref. 23) in n-hexane compared with stilbene.

Compound	ϕ_F	ϕ_C	τ_F^{calc} (ns)	k_F (10^8 s^{-1})	ϕ_{nr}
St	0.036	0.43	0.09 ^a	4	0.964
2-StP	0.0008	0.25	0.007	1.1	0.999
3-StP	0.075	0.56	0.19	4	0.925
4-StP	0.0016	0.37	0.008	2	0.998

Note a. From Ref. 10.

yields resemble those of St. Contrary to this, for 2- and 4-StP in an inert solvent at room temperature, ϕ_F is much smaller, being of the order of 10^{-3} (St, ~ 0.04), and ϕ_C is 0.25-0.37 (St, ~ 0.45). Quenching experiments (Ref. 24), too, indicate a very short singlet lifetime for these two isomers - less than 50 ps - almost one order of magnitude smaller than for 3-StP. This indication is confirmed by the approximate theoretical estimation of the lifetimes (see Table 3). This estimation was made by taking the experimental ϕ_F and the natural lifetime τ_F^o evaluated from the oscillator strength f (calculated by an INDO/S method) and the electronic transition energy ν ($f \propto 1/\nu^2 \tau_F^o$), using the St molecule as a reference (Ref. 20). The faster radiationless deactivation of 2- and 4-StP is not due only to a relatively fast rotation (smaller thermal barrier compared to St and 3-StP). In fact, the presence of n, π^* states could open new radiationless paths in azastilbenes, namely IC and ISC, particularly in the ortho and para aza-derivatives. The meta isomer, 3-StP, behaves differently since it has near nodes in the meta positions in both π and π^* orbitals (Refs. 6, 20, 22). This precludes intercombinational transitions between the n, π^* and the lowest π, π^* state. Theoretical calculations (Ref. 20) have shown that ISC occurs at a much faster rate in 2- and 4-StP, compared with St and 3-StP, but is not fast enough to compete effectively in fluid solution at room temperature with the fast internal rotation of the $^1\text{trans}^*$ form towards the reactive perp configuration. That ISC is almost negligible in fluid solvents was also confirmed by preliminary pulse radiolysis and laser flash photolysis experiments which indicated a triplet yield approaching undetectable limits (Ref. 25). On the other hand, a fast IC is the main deactivation path of pyridine (Ref. 26) and could also be partly operative in 4-StP and particularly in 2-StP at room temperature, possibly facilitated by the fact that twisting about the central double bond leads to a decrease of the S_1-S_0 energy gap. Only in viscous solvents or, better, in a rigid matrix at 77 K, when the concurrent $\text{trans} \rightarrow \text{cis}$ isomerization is inhibited, does IC probably also become a negligible process whilst here an efficient ISC may become operative (see also Ref. 20). This was indirectly proved by fluorescence quantum yield measurements at 77 K. The yield, in fact, is practically unity for St and 3-StP but remains markedly lower for the other two isomers in an inert solvent such as EPA (40% for 2-StP and 20% for 4-StP). It is to be noted that ϕ_F at 77 K increases noticeably in a polar medium like EPA where the value, slightly λ_{ex} -dependent, is high for all isomers (1.0, 0.92 and 0.87 for 2, 3 and 4-StP, respectively (Ref. 27)). Our working hypothesis is, therefore, that both radiationless processes contribute to the deactivation of StP's to an extent depending on temperature and solvent characteristics (polarity and viscosity). The IC probably makes an important contribution at room temperature and ISC becomes important only when the photoisomerization rate in an inert solvent is negligible. The increase in energy of the n, π^* states in polar media lowers both the radiationless unreactive processes (IC and ISC). The slowing down of IC at room temperature leads to an increase of the isomerization rate which reaches the high value of ~ 0.5 even for 2-StP. The reduction of ISC at low temperatures leads to an increase in ϕ_F at 77 K, as observed in EPA. It is to be noted that the 3 isomer, which seems not to be influenced by the n, π^* states, behaves differently in polar solvents, showing a decrease in ϕ_C at 298 K and a slight decrease in ϕ_F at 77 K. In this case, too, we carried out a study of the Arrhenius parameters using the temperature effect on the fluorescence quantum yields. The results are summarized in Table 4. Eq. 1 had to be modified, at least for the 2 and 4 isomers, to include IC as a possible activated process.

TABLE 4. Limiting fluorescence parameters (at 77 K) and Arrhenius parameters (A_F , s^{-1} , ΔE_F , kcal mol $^{-1}$) obtained from the temperature effect on fluorescence quantum yield (in the range 150-300 K) in two solvents.

Solvent	3-MP				EPA			
	ϕ_F^{lim}	τ_F^{lim}	$\log A_F$	ΔE_F	ϕ_F^{lim}	τ_F^{lim}	$\log A_F$	ΔE_F
St	1.00	1.5	12.6	3.2	1.00	1.5	12.8	3.2
2-StP	0.4	0.5	13.6	2.0	1.00	1.0	13.8	2.6
3-StP	1.0	1.4	12.3	3.3	0.92	1.5	12.6	3.5
4-StP	0.2	0.3	12.2	0.8	0.87	1.0	13.9	2.4

The ΔE_F values would thus represent a barrier both to twisting about the ethylene bond leading to isomerization, and to IC to S_0 , possibly through n, π^* states. The barrier is smaller for the 2 and 4 isomers that have been reported to isomerize with a negligible ΔE_C (Ref. 23). The general behaviour is similar to St and contributes to indicate that a similar singlet mechanism is operative, with a concurrent IC for the 2 and 4 isomers. The very low barrier for 4-StP in 3-MP could indicate a partial contribution of ISC to isomerization, even if the measurements were less reliable in this particular case because of the intervention of associative phenomena for this compound in 3-MP at low temperatures (Ref. 28). In a polar matrix of EPA, the IC should be negligible even for the 2 and 4 isomers. This is supported by the higher A_F values but not by the ΔE_F values which tend to increase for 2- and 4-StP instead of decreasing. Further work is in progress to clarify this point.

Dipyridylethylenes

Internal conversion seems to be the main decay path for diazastilbenes, i.e. the 1,2-dipyridylethylenes (DPE's), especially when the heteroatom is in the ortho or para positions. Theory predicts that in the three symmetrical isomers the lowest excited singlet state is again ethylenic, that the n, π^* states lie at least 0.3 eV above it and that there is a strong mixing between S_1 and the pyridinic states located nearby (Ref. 20). This produces an efficient IC to S_0 . The spin-orbit coupling has been evaluated and leads to ISC rate parameters not far from those of StP's, here again the lowest value being that of the meta compound (Ref. 20). Both fluorescence and photoreaction have very low quantum yields (except for meta isomers, where the yield is intermediate) and the reaction has to be sensitized by energy or charge transfer (see below) in order to obtain high yields of photoisomerization. Meta compounds are less prone to non-radiative decay, since they have both $\phi_F + \phi_C$ - for trans compounds - and $cis \rightarrow trans$ isomerization + cyclization quantum yields ($\phi_T + \phi_{cycl}$) - for cis compounds - higher than the corresponding ortho and para isomers. This is also shown by a comparison of the ϕ_F values of 3,3'-DPE at room and liquid nitrogen temperatures in EPA ($\lambda_{ex} = 313$ nm) ($\phi_F = 0.12$ and 0.75 at 298 and 77 K, respectively) with those for 4,4'-DPE ($\phi_F = 0.0004$ and 0.16 at 298 and 77 K, respectively) (Ref. 6 and present work). Here again, as in the case of St and StP's, ISC probably becomes operative in a rigid matrix at low temperatures when the isomerization does not occur.

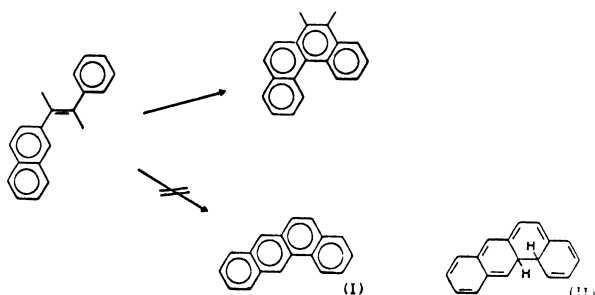
CIS DIARYLETHYLENES

As to the photoreactivity of the generally non-fluorescent cis compounds, there is competition between $cis \rightarrow trans$ isomerization and cyclization to dihydropolycyclic compounds (dihydrophenanthrene, DHP, in the case of St). The latter unstable intermediate loses hydrogen by the well-known oxidation reaction which takes place in the presence of hydrogen acceptors like oxygen, iodine, $FeCl_3$, etc., giving the final aromatic polycyclic compounds (Ref. 29). Only at low temperatures and high viscosities, when the yields of both isomerization and cyclization fall off on cooling (both photoreactions are believed to occur in the singlet manifold), does the fluorescence quantum yield become appreciable

and may reflect the main deactivation path for cis molecules (see, e.g., Ref. 16).

Photodehydrocyclization

Photocyclization provides a convenient route to polycyclic aromatics and to heterocyclic ring systems. In fact, for synthetic purposes, the chemical yield in inert solvents is satisfactory in most cases investigated and can be increased by a right choice of solvent (non-polar), of hydrogen acceptor (atomic iodine) and, not least, of the excitation wavelength; this latter can shift the photostationary state for the two geometrical isomers in favour of the cis form and avoid the back ring opening of the dihydro-derivative. Electron densities at the reactive positions, free valence indices and electronic overlap populations have all been used more or less successfully to predict the photoreactivity of these compounds, especially when diarylethylenes can photocyclize in several competitive parallel modes, thus giving different condensed-ring products (Ref. 29). One should note, however, that no benzanthracenes (I) were



obtained from 2-StN and its aza-analogues due to the known inertness towards ring closure leading to highly quinoid structures of the intermediate (II) (Refs. 29-31). The 3-pyridyl-derivatives give two cyclization products, depending on the orientation of the pyridine ring. Only very small amounts of phenanthrene analogues were obtained, however, when the nitrogen atom was in ortho position to the reaction centre, probably because the electron withdrawing effect of the heteroatom is such that there is insufficient electron availability at the position (or at the two positions, in the case of 3,3'-DPE) where the new bond has to be formed (Refs. 29,31,32).

As to the quantum yields of photoreaction, two types of measurement are reported in the text, referred to as ϕ_{DHP} and ϕ_{cycl} . The first value, taken from the literature (Ref. 16) refers to the yield of the primary photoprocess (formation of the intermediate dihydrophenanthrene analogue). The second value (used in this laboratory) refers to the formation of the final phenanthrene analogue in air-equilibrated solutions. Generally, the two sets of values are consistent.

Compared to St, the naphthyl derivatives, both symmetrical and asymmetrical, have relatively high yields of DHP formation and low yields of isomerization in the case of the more crowded cis 1-naphthyl compounds, whilst the contrary is true for 2-naphthyl compounds (see Table 2). For azastilbenes, ϕ_{cycl} is even smaller since -as said before - the electron withdrawing heteroatom reduces the photoreactivity (see Table 5). The yield is particularly low for

TABLE 5. Photocyclization quantum yields (ϕ_{cycl}) of styrylnaphthalenes (StN's), 9-styrylphenanthrene (9-StPh), styrylpyridines (StP's) (Ref. 32) and some n-pyridyl,9-phenanthryl-ethylenes (n,9-PPHE's) in n-hexane.

1-StN	0.17	4-StP	0.015
2-StN	0.03	9-StPh	0.25
2-StP	0.014	2,9-PPHE	0.08
3-StP	0.081	3,9-PPHE	0.22

the 2-StP (only one reactive position) and for the 4-StP (as reported in the literature, the formation of DHP is low for 4-pyridyl compounds (Ref. 33), probably because the photochemical and thermal ring opening is highly competitive with the ring closing process). For the 3-isomer, ϕ_{cycl} is the sum of the yields for the formation of two cyclic compounds corresponding to two rotational isomers. Calculations by the Hückel method have shown that the electron density on the reaction centre increases by excitation when the nitrogen atom is para to this centre and decreases when it is ortho to it (Ref. 32). Correspondingly, we found a sensibly smaller yield in the latter case for all compounds investigated (3-StP, 1,3-NPE, 2,3-NPE, 3,9-PPhE).

In polar solvents, the cyclization rate is drastically reduced, and in practice only trans formation was observed. The same is true for the protonated azastilbenes in acidic solutions. Again, as in the case of the trans compounds, the polar solvent could favour isomerization either by modifying the energy surfaces or by being involved in charge transfer interaction with the olefin, thus promoting triplet or ion-radical mechanisms.

BIMOLECULAR PROCESSES OF EXCITED DIARYLETHYLENES

Even if the fluorescent state of stilbene-like molecules is short-lived in most cases, it can generally be intercepted by suitable additives which, by reducing the fluorescence yield, can act as quenchers or sensitizers of the photoreaction. The sensitizing effect, which can become particularly important in those cases where the photoreaction quantum yield is very low, depends whether the decay takes place in the singlet manifold or through the triplet manifold. Three main types of interaction were studied.

Energy transfer

If triplet donor sensitizers have the required energy, they are well known to populate the T_1 state of diarylethylenes. The T-T energy transfer is generally an efficient process whose yield reaches the ISC yield of the donor when suitable concentrations of the two partners are used. From the triplet manifold, the olefin has almost the same chance of reaching the trans and cis ground state (Ref. 1). Benzophenone and anthraquinone were used successfully but the triplet energy of biacetyl ($E_T = 56.5 \text{ kcal mol}^{-1}$) was also sufficient for most trans isomers (Ref. 34). More than thirty stilbenes and azastilbenes have been studied. Cis-trans isomerization was the only photoprocess observed in practice, at least in the absence of oxygen. The trans \rightarrow cis photoconversion was studied in more detail and its quantum yield ϕ_C^{sens} was always found to be in the range 0.45 - 0.55. The yield can, therefore, be significantly increased for compounds of low inherent yield, as is the case of some dipyridylethylenes and other examples reported in Table 6.

TABLE 6. Sensitized (by biacetyl) trans \rightarrow cis photoisomerization quantum yields for stilbene analogues in benzene at room temperature compared to the yields for the direct photoisomerization in n-hexane (Ref. 34).

Acceptor	ϕ_C	ϕ_C^{sens}
2-StP	0.22	0.46
2-StN	0.12	0.46
3,3'-DPE	0.08	0.48
4,4'-DPE	0.003	0.45

Sensitization with triplet donors proved to be useful with cis compounds, too, when the preference was to photoselect the cis \rightarrow trans isomerization without concurrent cyclization.

Proton transfer

The protonation of the heteroatom of azastilbenes is characterized by pK_a values in the range 4 - 6 (Refs. 35,36). The DPE's have two basic centres; they

thus display a pK_a^I for the first protonation in the range 4.8-5.6 and a pK_a^{II} for the second protonation in the range 2.3-3.6 (Ref. 35b). The study of the photoisomerization of azastilbenes at different pH's is particularly interesting when the free base and the conjugate acid have greatly different photoreaction quantum yields, since the process can be quenched or enhanced by changing the pH from <3 to >7 . The latter value may not be sufficient to produce the behaviour of the free base if the hydrolytic reaction takes place also in the excited state. In fact, pyridine and quinoline derivatives become much stronger bases in S_1 . Application of the Förster cycle procedure to these molecules leads to pK_a^* values in the S_1 state being 6-8 pK units higher than those of the ground state. Fluorimetric titration has confirmed this high basicity ($pK_a^* \sim 12-13$) when the S_1 lifetime was long enough to permit the excited molecule to equilibrate, at least partially, with the proton (Refs. 35,36). In this case, one has to use $pH \sim 13-14$ in order to obtain the reaction of the neutral molecule. In fact, a two-step trend in the plot of ϕ_F and ϕ_C against pH was observed, the two inflection points corresponding to pK_a and pK_a^* (Fig. 3).

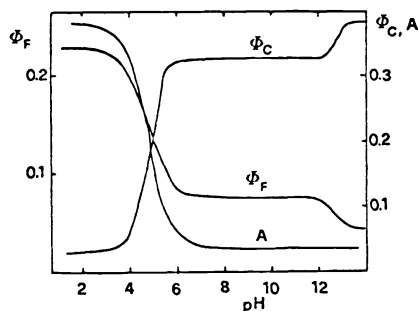


Fig. 3. Photoisomerization and fluorescence quantum yields and absorbance of trans 3-styrylpyridine as a function of pH in 9:1 water:ethanol ($\mu = 1$ by NaCl (ϕ_C) and Na_2SO_4 (ϕ_F)).

When the extent of the equilibration is particularly high (as happens for compounds of a relatively high singlet lifetime in strong proton donating media), there may be photochemical implications since both the fluorescence and photoisomerization quantum yields are often different for the neutral and protonated molecules. Thus, it may happen that the experimental ϕ_C in a neutral medium, i.e. in the pH range between the two pK_a 's, is intermediate between the values characteristic of the basic and acidic species, since a fraction of the excited molecules emits and isomerizes in the cationic form, despite the fact that only the free base is directly excited (see Fig. 3 and Ref. 37). As an example, the following parameters were found for 3-StP (Refs. 35a,38):

ϕ_F^a	ϕ_F^b	τ_F^a	τ_F^b	$k(10^8 s^{-1})$	$k(10^9 M^{-1} s^{-1})$	$k_{NH_4^+}(10^8 M^{-1} s^{-1})$	$k_{NH_3}(10^5 M^{-1} s^{-1})$
0.21	0.04	5.5	0.9	2.0	10.0	9.0	8.1

where the superscripts a and b indicate the acidic and basic forms, respectively, and the rate parameters refer to the forward and back reactions of the protolytic equilibrium, using H_2O and NH_4^+ as proton donors. Table 7 shows the

TABLE 7. Photoisomerization quantum yields of 3-StP and two 4'-X-substituted derivatives in 9:1 water:ethanol at different pH's ($\mu = 1$, by NaCl)(see Ref. 37).

4'-X	pH = 2	pH = 8	pH = 14
H	0.03	0.33 (17)	0.38
CH ₃	0.04	0.33 (34)	0.37
OCH ₃	0.0006	0.29 (20)	0.42

ϕ_C values of 3-StP and some of its derivatives at low and high pH -where they are present in solution as 100% acidic and 100% basic forms, respectively -

and at neutral pH, where a certain extent of excited state equilibration with the proton (shown in brackets as percentage of acidic form still present at pH = 8) was detected by fluorimetry.

Charge transfer

The charge transfer interaction of excited stilbenes with amines (donors) in non-polar solvents leads to the formation of fluorescent exciplexes, which often induces ISC of the acceptor olefins and consequent isomerization in the triplet manifold. Parallel photoaddition reactions by tertiary amines in polar aprotic solvents and by secondary amines in all aprotic solvents, take place with a much smaller quantum yield and were neglected in the present context (Ref. 39). The experimental quantum yield of photoisomerization (ϕ_C), in proportion, is reduced less than ϕ_F . Its value is the sum of two contributions: by the acceptor free molecules (ϕ_{CM}) and by the molecules which react through the complex (ϕ_{CE}). The latter limiting value (ϕ_{CE}^{lim}) can be evaluated at large quencher concentrations $[Q]$, when practically all molecules are in the complexed form, or obtained by extrapolation to $[Q] \rightarrow \infty$ of the plots of $1/\phi_{CE}$ against $1/[Q]$ (Ref. 40). No increase of the isomerization yield was obtained from these exciplexes with amines, the ϕ_{CE}^{lim} values being similar or smaller than those of the inherent ϕ_C . The presence of a nitrogen atom in the ring does not markedly lower the reduction potential of the hydrocarbons but lowers it enough to make them better electron acceptors. However, IC is important for many azastilbenes even in the complexed form so that both fluorescence and isomerization of the complex have low quantum yields (Ref. 40).

The interaction of azastilbenes with inorganic anions as donors (alkali halides and thiocyanates) leads to the formation of short-lived non-fluorescent complexes. The absence of radiative decay of the complex leaves more chances for radiationless transitions to be induced, ISC being particularly favoured when the anion has a high atomic weight and the olefin acceptor has a high inherent ϕ_{ISC} (Ref. 41). As all these molecules have been shown to be reactive at the triplet level, an increase in triplet population by suitable additives can lead to a marked increase in the photoreaction quantum yields of compounds with low inherent yields. Significant examples are reported in Table 8.

TABLE 8. Stern-Volmer coefficients (K_Q , M^{-1}) and inherent fluorescence and photoisomerization quantum yields of some azastilbenes compared to the reaction yields induced by their complexes with inorganic anions^a (see Refs. 41,42).

System	ϕ_F	ϕ_C	K_Q	ϕ_{CE}^{lim}
3-StP + I ⁻	0.029	0.44	4.1	0.52
3-StPH ⁺ + I ⁻	0.21	0.27	39.0	0.25
3-StPH ⁺ + Br ⁻	0.21	0.27	19.0	0.04 ₅
4'-OCH ₃ -3-StPH ⁺ + I ⁻	0.012	0.0006	2.0	0.36
3,3'-DPEH ₂ ⁺⁺ + Br ⁻	0.033	0.045	4.3	0.50
3,3'-DPEH ₂ ⁺⁺ + Cl ⁻	0.033	0.045		0.00

Note a. Solvent: 9:1 water:ethanol, except for the system 3-StP + I⁻ (2:3 acetonitrile:water).

Considering that the sensitized photostationary state measurements in the presence of high energy triplet donors result in ~50% of the cis isomer for most azastilbenes, one can estimate that the quenching by halides leads to the formation of the reactive triplet with an efficiency going from ~8% in the complex (3-StPH⁺ + Br⁻) to ~100% in the case of (3,3'-DPEH₂⁺⁺ + Br⁻). In the latter case, ϕ_{CE}^{lim} is increased 15-fold compared to ϕ_C in the absence of a quencher. In the system (4'-OCH₃-3-StPH⁺ + I⁻), the increase is 600-fold.

CONFORMATIONAL ISOMERS OF DIARYLETHYLENES

Fairly recently, evidence has been given for the existence, in solutions of stilbene-like molecules, of an equilibrium between rotational conformers involving the quasi-single bonds between the aromatic groups and the ethylenic carbon atoms (Refs. 43-45). The combination of the two effects, the tendency towards coplanarity of the delocalized π system and the steric repulsion in planar forms, leads to potential minima in the quasi-planar configurations, separated by an energy barrier. The presence of a substituent or a heteroatom in the ortho or meta positions of St or the presence of polycyclic groups attached to the central double bond gives rise to two (in some cases, also three or four) possible rotamers. Absorption and emission properties of the postulated rotamers can be different to greater or lesser extents. Therefore, the fluorescence behaviour does often depend on both excitation and emission wavelengths. Selective photoexcitation can also influence the photoreactivity of the system. A large variety of diarylethylenes having quasi-planar conformations with a similar steric interaction (almost isoenergetic) have been shown to display pronounced changes in the emission spectrum with λ_{ex} , even in fluid solution at room temperature. Moreover, in many cases the fluorescence is not mono-exponential. Two decay components are generally observed except in those cases where only one species predominates in solution (smaller steric repulsions) or when two or more species have too similar or too short a lifetime, making the separation of distinct components practically impossible. When large energy differences are expected among different conformers and one of them is expected to predominate in solution, no changes of fluorescence spectra with λ_{ex} are exhibited (this is the case of 1-StN, 9-StPh, etc. in fluid solvents; see Ref. 43 and present work). In such cases, and in general when the anomalies are very small at room temperature (e.g., when the rotation of a pyridyl group is involved) (Refs. 27,46), study is facilitated by the use of a rigid matrix at low temperature where the spectra are sharper and the luminescence yield is generally higher due to the absence of concurrent trans \rightarrow cis photoisomerization. It should be noticed that all stilbene-like molecules, even when the 180° rotation about the single bond gives identical conformers (e.g., St, 4-StP), display a slight λ_{ex} -dependence in a rigid matrix at liquid nitrogen temperature (Refs. 27,46). In these cases, the existence of conformers is probably due to matrix-stabilized average conformations differing by the disrotatory (or conrotatory) twisting of the two aromatic groups with respect to the plane of the double bond.

Azastilbenes

The azastilbenes show very slight anomalies at room temperature. The analysis based on the vibronic structure permits a separation between the two species to be performed only from the spectra in matrices. Fig. 4 shows, as an example,

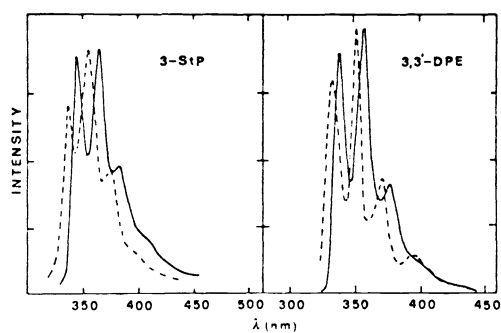
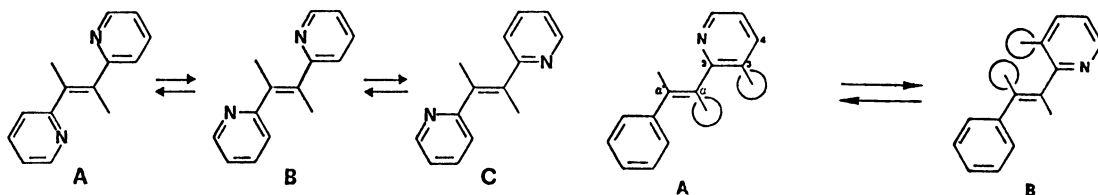


Fig. 4. Fluorescence spectra of almost pure conformers of trans 3-StP and 3,3'-DPE in EPA at 77 K (solid curve: conformer A; dashed curve: conformer B).

the almost pure emission spectra at 77 K ascribed by us to two conformers of 3-StP and 3,3'-DPE. The red shifted spectrum of species A (generally, shorter-lived) was obtained by excitation at the long wavelength edge of the absorption spectrum. The emission spectrum of species B was obtained by difference from the spectrum of the mixture A + B (see Refs. 27,46). The fluorescence spectra

of A and B thus obtained, similar in shape but slightly shifted in energy (the shift depends on the position of the heteroatom and on the solvent) are clearly superposed in the original experimental spectra. Moreover, a combination of the excitation peaks of A and B corresponds nicely to the absorption spectrum of the starting compound (mixture of conformers). The NMR chemical shifts of the ethylenic protons, calculated considering the ring anisotropy, the electric and magnetic effects of the heteroatom and the π charge variations, are very sensitive to molecular conformations (Ref. 47). Only structure A of 2,2'-DPE gave values comparable with the experimental ones and probably pre-



vails in solution. Similarly, the preferred conformation of 2-StP should be A, where the steric interaction should be smaller. Even the small change in the chemical shift with the solvent in the case of the ethylenic protons has been explained as being due to their strong interaction with the nitrogen lone pair, so that the solvent displays only a minor influence. This reflects the coplanarity of the pyridine ring with the ethylene plane and therefore its restricted rotation (Ref. 47). Considerations based on a dipole moment study (Ref. 48) also led to the conclusion that A and B should be equally probable for 3-StP, whilst the less crowded conformation (tentatively assigned to the red shifted A spectrum) should be favoured in 2-StP. In fact, the λ_{ex} dependence, and therefore the presence of the two species, is slightly more evident for 3-StP.

Naphthyl derivatives

Naphthyl analogues of St are particularly suitable for a study of conformational equilibria. The fluorescence anomalies are in fact observable even at room temperature. A fluorescence analysis, based on observations of ϕ_F and τ_F at different λ_{ex} and λ_{em} and on reasonable assumptions about the absorption properties of the conformers, allowed the photophysical parameters of the two components to be evaluated from those of the mixture (Ref. 45). The lifetime determination involves observations of the monochromatic fluorescence response function for the mixture

$$\bar{i}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (3)$$

The properties of the two fluorescent species are indicated by subscripts 1 and 2, the first species being taken as that with a shorter lifetime ($\tau_1 < \tau_2$). Note that

$$A_i = f_i(\lambda_{\text{ex}}) F_i(\lambda_{\text{em}}) k_i \quad (4)$$

where f_i are the fractions of excited molecules belonging to each species, F_i is the fluorescence intensity and $k_i = 1/\tau_i$. Deconvolution analysis of the decay curve (measured at isoemissive λ_{em}) leads to the evaluation of the fluorescence lifetimes of the two species and the ratio of the pre-exponential factors. These data are reported in Table 9 at two λ_{ex} for two naphthyl-derivatives. The fractions of excited molecules belonging to each species

$$f_i = \epsilon_i(\lambda_{\text{ex}}) c_i / \bar{\epsilon}(\lambda_{\text{ex}}) \bar{c} \quad (5)$$

where the barred symbols refer to the properties of the mixture, can thus be obtained, and are also shown in Table 9. These data allow the fluorescence quantum yields and the relative absorption spectra of the two components to be calculated. On the reasonable assumption that the Franck-Condon envelopes of the first absorption band systems are similar in shape for the two conformers, it is to be expected from the radiative lifetime relation that

$$(\epsilon_1)_{00}/(\epsilon_2)_{00} \approx \tau_{F_2}^0/\tau_{F_1}^0 = \phi_{F_1} \tau_2 / \phi_{F_2} \tau_1 \quad (6)$$

From the relative absorption spectra one obtains $(\epsilon_1)_{00} c_1 / (\epsilon_2)_{00} c_2$ which com-

TABLE 9. Fluorescence parameters obtained from lifetime measurements of 2-StN and 2,2-NPE in n-hexane at room temperature (see Ref. 45 and present work) at two excitation wavelengths (λ_{ex} , nm).

Fluorescence parameters	2-StN		2,2-NPE	
	$\lambda_{\text{ex}}=315$	$\lambda_{\text{ex}}=350$	$\lambda_{\text{ex}}=315$	$\lambda_{\text{ex}}=356$
τ_1 (ns)	5.1	5.4	1.4	1.2
τ_2 (ns)	27.6	25.6	8.5	8.5
A_1/A_2	0.75	7.31	3.8	21.8
f_1	0.12	0.58	0.37	0.77
f_2	0.88	0.42	0.63	0.23

combined with the previous equation gives the conformer concentrations. Two rotamers were detected in both examples of Table 9 though four species are conceivable for the aza-derivative. The latter appears to behave as a two-component system since the effect of the "naphthyl rotamers" probably predominates over the "pyridyl rotamers". Table 10 shows the photophysical properties of these

TABLE 10. Photophysical parameters of the two conformers of 2-StN and 2,2-NPE in n-hexane at room temperature, as derived from the analysis.

Photophysical parameters	2-StN		2,2-NPE	
	species 1	species 2	species 1	species 2
ϕ_F	0.83	0.50	0.015	0.11
τ_F (ns)	5.1	27.6	1.3	8.5
k_F (10^7 s^{-1})	16.0	1.8	1.1	1.3
k_{nr} (10^7 s^{-1})	3.3	1.8	75.7	10.6
relative abundance	0.24	0.76	0.74	0.26

conformers as derived from the analysis. Nice confirmation of the reliability of the analysis comes from differential quenching experiments by O_2 , KI, etc. In fact, these experiments show a preferential quenching of the longer-lived component. Fig. 5A shows that the excitation spectrum of 2,3-NPE obtained at

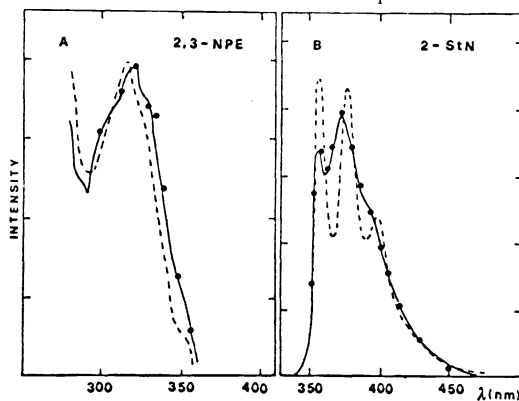


Fig. 5. A) Excitation spectrum of 2,3-NPE in n-hexane; dashed line: mixture; full line: with $[\text{O}_2] = 1.5 \times 10^{-2} \text{ M}$; spots: species 1 from analysis. B) Emission spectrum of 2-StN in 3:2 water:acetonitrile; dashed line: mixture at $\lambda_{\text{ex}}=310 \text{ nm}$; full line: with 0.3 M NaI ; spots: species 1 from analysis.

$[O_2] \sim 1.5 \times 10^{-2} M$ is practically identical in intensity distribution with the absorption spectrum of the much less quenched short-lived species $[\xi_1(\lambda_{ex})c_1/\bar{c}]$. Correspondingly, Fig. 5B shows that the fluorescence spectrum of 2-StN obtained at $[KI] = 0.3 M$ is practically identical with the fluorescence spectrum of the short-lived component $[F_1(\lambda_{em})]$ as derived from the analysis.

Cis compounds

It is more difficult to obtain information on conformers for the non-fluorescent cis compounds. Different photodehydrocyclization products (see above) are expected and found from different conformations. However, a simple investigation, only based on the composition of the photoreaction mixture, would not be very informative since different products are expected even if free rotation were operative. Moreover, the ratio of the final polycyclic compounds is very dependent on experimental conditions, like the solvent, the oxidant and, particularly, the excitation wavelength (reversible ring opening of the DHP analogue towards the starting cis isomer) as well as on the conformer composition. Some reliable information could be obtained only from a flash photolysis study on the DHP analogue intermediates as a function of temperature, since a shift of the conformational equilibria on cooling can be brought to light by the changes in the mixture of the primary photoproducts. In all our experiments, both on a preparative scale and for quantum yield determination, when more than one cyclization product was expected, we always succeeded in obtaining them with the exception - as said above - of the final compounds of anthracenic structure, that were always absent from the photoproducts. Sometimes, however, the latter were obtained with a small yield (see, e.g., the negative effect of a nitrogen atom in ortho position with respect to the reactive centre) (see Refs. 29,31,43,49).

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