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Excited State Reactivity of Aza Aromatics. 9. Fluorescence and Photoisomerization of Planar and Hindered Styrylpyridines

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The effect of methyl substitution at the ethylenic bridge on the fluorescence and trans → cis photoisomerization of styrylpyridines (StP's) has been investigated. As compared with the unsubstituted planar olefins, steric hindrance modifies the shape of the potential energy barrier for photoisomerization. The hindered compounds show a marked decrease in the fluorescence quantum yield. A parallel decrease in the photoreaction quantum yield has been observed for the α-methyl derivatives of stilbene and 3-StP. Temperature and solvent effects on planar and hindered StP's give interesting information on the intramolecular rotation in excited azastilbenes and its competition with the other deactivation pathways. While intersystem crossing is negligible in fluid solvent, it becomes competitive with fluorescence in high viscosity media. The photoisomerization mechanism is discussed on the basis of the model available for stilbene.

Introduction

Experimental observations have recently established that the unsubstituted stilbene (St) isomerizes in the singlet manifold.[1] The internal rotation about the central double bond (angle ϑ) is an activated process which competes with fluorescence emission from the planar trans configuration while $S_1 \rightarrow T_1$ intersystem crossing (ISC) has a very low efficiency, at least in inert nonviscous solvent.[1,2] On the basis of theoretical predictions,[3] the rotation leads to a crossing from the lowest excited ($^1B_u^*$) state to a doubly excited ($^1A_g^*$) state.[4] The latter exhibits a potential energy minimum near the perpendicular (perp) configuration from which fast internal conversion (IC) to the maximum of the S_0 curve and decay to its trans and cis sides takes place.

Steric crowding in the vicinity of the ethylenic bridge of St noticeably affects the photophysical and photochemical behavior of the trans isomer which becomes similar to that of the cis isomer due to the common property of inhibited coplanarity caused by the substituents. Steric interaction of the ortho hydrogens with the substituted ethylenic bridge is relieved by twisting about the exocyclic single bonds.[5] This induces changes in the potential energy profile for twisting about the α–α' central double bond thus affecting the rate for geometrical photoconversion. In particular, the fluorescence and direct photoisomerization quantum yields of trans α-CH_3St and α,α'-$(CH_3)_2$St are much less sensitive to viscosity and temperature than are the corresponding parameters of trans St.[6] This indicates that the energy barrier existing in St is drastically reduced in the hindered compounds.

Introduction of a nitrogen atom in the ring remarkably affects the excited state behavior of St.[7] It thus seemed interesting to investigate the effect of α-CH_3 substitution in the three isomeric styrylpyridines (StP's). The results obtained so far on the fluorescence and photoisomerization of the α-CH_3 derivatives of StP's and some new results on the temperature effect for the unsubstituted StP's are reported and discussed on the basis of the model available for St.

Experimental Section

The compounds investigated were synthesized by standard procedures,[8] with the exception of α-CH_3-3-StP.

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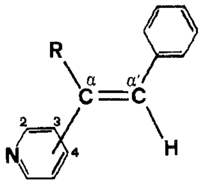

R = H or CH_3

Two routes were followed for the synthesis of the latter compound. The starting material, 3-acetylpyridine, was allowed to react with the ylid obtained from benzyltriphenylphosphonium bromide (a mixture of 50:50 geometrical isomers was thus obtained) or with benzyl magnesium bromide. In the latter case, dehydration was made in the presence of traces of $KHSO_4$ at 100–120 °C (a prevalence of trans isomer was thus obtained). The two geometrical isomers were then separated by column chromatography. Further details on the preparation and purification will be given elsewhere.[9]

The solvents were Carlo Erba chemicals. *n*-Hexane, RS grade, was used without further purification. 3-Methylpentane (3-MP) and glycerol, of reagent grade, were purified by standard procedures.

Absorption spectra at room and low temperature were recorded on a Cary 17 spectrophotometer. The spectra of the cis isomers were corrected for the amount of trans (2–4%) determined by gas chromatography.

Fluorescence measurements were made with a MPF-44 Perkin-Elmer spectrophotofluorimeter with an accessory for spectrum correction using rhodamine B as quantum counter (λ_{ex} = 260 nm in *n*-hexane and 315 nm in water-ethanol and glycerol; for the measurements in rigid matrix λ_{ex} was around 305 nm for the unsubstituted compounds and 280 nm for the α-CH_3 derivatives, corresponding to absorption maxima or minima). For determination of the fluorescence quantum yields ϕ_F (three–four independent experiments; mean deviation 2% in fluid solution, 10% in glycerol and in rigid matrix), the standards used were α-NPD in cyclohexane solution (ϕ_F = 0.58)[10] and 9,10-diphenylanthracene in 3-MP rigid solution at 77 K (ϕ_F = 1).[11] Differences in the low ϕ_F values with respect to those previously reported[7] are due to variations with λ_{ex} and/or to improved experimental conditions. Measurements in glycerol were done in the presence of 1% ethanol for solubility requirements and in the presence of 4% aqueous Britton buffer (pH ~9) to avoid interaction of the protic solvent with the heterocyclic nitrogen.

Photoreaction measurements were performed by use of a 313-nm excitation radiation, isolated from a stabilized Osram HBO 200-W high-pressure mercury lamp by a Balzers interference filter with half-band width of 10 nm. The trans → cis photoisomerization was studied as reported in a previous paper.[7] The quantum yields reported in the tables are the mean of at least three independent experiments; the mean deviation was 4% for the measurements in fluid solutions and 6% for those in rigid matrices.

All measurements were made in air-equilibrated solutions as oxygen has a negligible effect.

Results and Discussion

As found for St,[6] noticeable differences in the photochemical and spectroscopic behavior of planar and nonplanar molecules are observed for the azastilbenes under study.

Spectra. Table I reports the maxima of the longer wavelength absorption band at room temperature and of both absorption and fluorescence bands in a rigid matrix at 77 K for the α-CH_3StP's. As in the case of α-CH_3St,[5] the absorption spectra of the sterically hindered azastilbenes show a loss of vibrational fine structure as well as hypsochromic and hypochromic shift of the first intense band. The hindered trans isomers resemble the unsubstituted cis isomers in the position of the band but the intensity of the band remains rather higher. The loss of structure is shown also by the fluorescence spectra as expected for nonplanar excited states. The Stokes shifts are difficult to measure in fluid solutions at room temperature because of the very low emission intensity of these hindered compounds. Compared to α,α'-dimethylstilbenes,[12] the shifts are expected to be relatively smaller, the relaxation processes following the electronic transition playing probably a less important role in the less overcrowded α-methyl derivatives. In a rigid matrix, the shifts become negligible as the medium prevents the excited molecule from relaxing to a conformation of less steric strain.

TABLE I: Spectral Parameters (λ_{max} in nm) for Absorption and Fluorescence of α-CH_3 Derivatives of Stilbene and Styrylpyridines in Inert Solvent

	n-hexane (T = 298 K)		3-methylpentane (T = 77 K)	
compd	trans, λ_{max}^{abs} (log ϵ_{max})	cis, λ_{max}^{abs} (log ϵ_{max})	trans, λ_{max}^{abs} (log ϵ_{max})	trans, λ_{max}^{fl}
α-CH_3St	273 (4.32)	263 (4.07)	280 (4.44)	361
α-CH_3-2-StP	290 (4.25)	283 (3.96)	276 (4.21)– 300 (4.32)	364
α-CH_3-3-StP	270 (4.21)	260 (4.05)	282 (4.21)	364
α-CH_3-4-StP	275 (4.26)	263 (3.98)	293 (4.25)	369

TABLE II: Fluorescence and Trans → Cis Photoisomerization Quantum Yields of Stilbene Analogues in *n*-Hexane at 298 K and in 3-Methylpentane at 77 K

	T = 298 K		T = 77 K	
trans isomers	ϕ_F	ϕ_C	ϕ_F	ϕ_C
St	0.036 (0.040)[a]	0.41 (0.50)[c]	1.0	0
2-StP	0.0008 (0.003)[b]	0.25 (0.25)[b]	0.40	0
3-StP	0.075 (0.070)[b]	0.56 (0.43)[b]	1.0	0
4-StP	0.0016 (0.005)[b]	0.37 (0.37)[b]	0.20	0
α-CH_3St	$<6 \times 10^{-4}$ (0.003)[c]	0.27 (0.48)[c]	0.13	0.14
α-CH_3-2-StP	$<6 \times 10^{-4}$	0.23	0.38	0.09
α-CH_3-3-StP	$<6 \times 10^{-4}$	0.38	0.42	0.08
α-CH_3-4-StP	$<6 \times 10^{-4}$	0.36	0.23	0.10

[a] From ref 1 (solvent, *n*-pentane). [b] From ref 13 (benzene). [c] From ref 6 (methylcyclohexane–isohexane for St, isohexane for α-CH_3St).

The solvent effect on the absorption is small with the exception of the isomer 4 which displays relatively stronger bathochromic shifts in polar solvent. Even the temperature effect is small, the absorption spectra at 77 K being only slightly red shifted.

Quantum Yields. Fluorescence (ϕ_F) and trans → cis photoisomerization (ϕ_C) quantum yields of α-CH_3StP's in an inert solvent at room and liquid nitrogen temperature are reported in Table II. The corresponding values for St and unsubstituted StP's are also reported for comparison. The ϕ_F and ϕ_C values for StP's in Table II are in good agreement with our previous data in the same solvent[7] and with those of Whitten et al. in benzene.[13] However, our ϕ_C value for St and ϕ_F and ϕ_C values for α-CH_3St are rather smaller than those reported by Fischer.[6]

A general scheme describing the deactivation pathways of the first excited singlet state of trans geometry (planar, $\vartheta = 0°$, in the nonhindered compounds) is as follows. The deactivation of ^{1}trans can occur through ISC to the triplet ^{3}trans, through IC to the ground state ^{0}trans, fluorescence, and through internal rotation toward the perpendicular

Scheme I

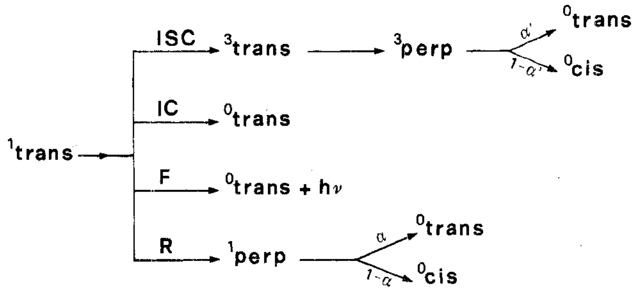

TABLE III: Temperature Dependence of ϕ_C for StP's in n-Hexane

trans isomers	ϕ_C			
	+60 °C	+25 °C	−10 °C	−60 °C
St	0.41	0.41		0.22
2-StP	0.25	0.25	0.25	0.26
3-StP	0.55	0.56	0.41	0.34
4-StP	0.37	0.36	0.34	0.37
α-CH_3St		0.27		0.26
α-CH_3-2-StP		0.23		0.26
α-CH_3-3-StP		0.38		0.37
α-CH_3-4-StP		0.36		0.34

configuration (ϑ = 90°) (Scheme I). In principle, isomerization can occur in the triplet manifold (triplet mechanism) or from the twisted singlet state (singlet mechanism), the relative importance of the two mechanisms depending on the nature of the substituents and experimental conditions.[1,6,7]

Styrylpyridines. As previously observed,[7] Table II indicates that the fluorescence and photoisomerization quantum yields for 3-StP in an inert solvent are even higher than for St, while isomer 4, and mainly isomer 2, are characterized by lower yields for both emission and photoreaction and correspondingly by faster radiationless deactivation paths. Quenching experiments indicate a very short singlet lifetime for these two isomers, less than 100 ps, almost one order of magnitude shorter than for 3-StP.[14] It should also be recalled that the behavior of 3-StP is unusual since ϕ_F depends on λ_{ex} across the first intense absorption band.[15] However, the present measurements (Table II) were made at λ_{ex} where the effect is minimized and appears to be self-consistent.

The temperature effect on photoisomerization in the range 213–333 K (Table III) shows that, while ϕ_C of 3-StP decreases with temperature similarly to St (with an activation energy of ~2.5 kcal mol^{-1}), it remains practically constant for isomers 2 and 4 ($\Delta E \simeq 0$). This implies that the presence and position of the nitrogen atom markedly affects the potential energy surfaces as a function of ϑ. The absence of a thermal barrier in the internal rotation of isomers 2 and 4 is expected to lead to higher rate parameters for the "horizontal"[2a] trans → perp process.

Another peculiar behavior of these molecules is shown in Table II. While preliminary measurements indicate that the fluorescence lifetime in rigid matrix at the liquid nitrogen temperature is almost the same (about 1.5 ns in EPA) for both St and its aza derivatives, indicating that the emission originates from a similar (π,π^*) state, the fluorescence quantum yield at 77 K is practically unity for St and 3-StP but it is only 40 and 20% for isomers 2 and 4, respectively.

The different behavior of the last two isomers could be due to the presence of low-lying (n,π^*) states which favor radiationless deactivation, in particular when the heteroatom is in the ortho or para positions.[7,16-18] This does not happen when the heteroatom is in the meta position since both the π HOMO and LUMO have near nodes at this position, thus making intercombinational transitions between (n,π^*) and (π,π^*) states much less probable.

TABLE IV: Quantum Yields of Photoisomerization and Photocyclization and Decay Fractions from the Singlet Pathway for StP's in n-Hexane

compd	ϕ_C	ϕ_T[a]	ϕ_{cycl}[b]	α
St	0.41	0.29	0.075	0.42
2-StP	0.25	0.24	0.014	0.49
3-StP	0.56	0.22	0.081	0.28
4-StP	0.37	0.34	0.015	0.48

[a] From ref 7. [b] From ref 21.

It is not simple to discriminate whether the deactivation of isomers 2 and 4 is mainly attributable to IC or to ISC. In fact, recent pulse radiolysis and laser flash photolysis experiments in an inert solvent at room temperature have shown that ϕ_{ISC} of the three isomeric StP's is quite low, less than 1%.[19] This interesting information is in agreement with other data obtained in this laboratory which indicate a prevalent singlet mechanism for the trans → cis photoisomerization of StP's in an inert solvent.[7] Hence, we believe that the main process competitive with fluorescence in fluid media is internal rotation which would be particularly fast for isomers 2 and 4. The relatively low ϕ_C values for the last two isomers, particularly for isomer 2, could be thus explained by a relevant IC to S_0, probably after twisting (at $\vartheta > 0°$). In fact, the assumption of a negligible ϕ_{IC} for rigid aromatic hydrocarbons[10] is not necessarily valid for the flexible stilbene-like molecules whose S_1 potential energy may decrease when the angle of twisting around the ethylenic bridge increases, as found for St.[2,3] Correspondingly, the energy of S_0 increases so that the energy gap S_1–S_0 is reduced markedly and the probability of IC increases and reaches its maximum value in the region of ϑ = 90°.[20] The faster deactivation of isomers 2 and 4 can be thus explained by an IC which would be favored, as assumed before, by a deactivating role of the (n,π^*) energy profile somewhere along the reaction coordinate, in the range of $0° < \vartheta < 90°$.

It is interesting to examine the corresponding results for the back-isomerization. Table IV shows the quantum yields for the cis → trans photoconversion (ϕ_T) and for the photocyclization of the cis isomers (ϕ_{cycl}) compared to those for the trans → cis photoreaction. Also given in Table IV are the decay fractions from the twisted singlet configurations to the ^{0}trans (α) and ^{0}cis ($1 - \alpha$) side, calculated from the equation

$$\phi_T/\phi_C = (k_R'\tau_C/1 - \phi_F)(\alpha/1 - \alpha) \qquad (1)$$

where $k_R'\tau_C$ is equal to the quantum yield of the cis → perp process. The latter can be evaluated by knowing the competition between ring closing (cyclization) and twisting of the cis isomers. The available quantum yields for photocyclization of StP's refer to the formation of the final stable phenanthrene-like product. Thus, they represent only a minimum value for the quantum yields of formation of the dihydrophenanthrene which is the primary cyclization product of the cis isomers.[1] Use of these quantum yields (assuming $k_R'\tau_C = 1 - \phi_{cycl}$) in eq 1 results in the α values reported in Table IV. Perusal of the table shows that these decay fractions from the singlet manifold are different from those found from ^{3}perp (α' = 0.45 and 0.37 in benzene, approximately the same for the three isomeric StP's, from experiments sensitized by benzophenone[13] and anthraquinone,[22] respectively), particularly for isomer 3. Even if this result is not new,[1] it could indicate that the parameters introduced in the equation are not sufficiently precise or that caution is needed in the interpretation of the decay mechanism of ^{1}cis. Table IV indicates also that the sum $\phi_T + \phi_C$ for direct isomerization is far from unity, particularly for isomer 2. It remains too low even taking into account fluorescence from ^{1}trans and cyclization from ^{1}cis (both processes have very small yields for isomers 2 and 4). This fact, which invalidates the use of eq 1, could also imply, as hypothesized before, that IC to ^{0}trans and ^{0}cis partially occurs *before* the perp configuration. Further experimental work is required (particularly on the dihydrophenanthrene formation from ^{1}cis) before correctly interpreting the data at disposal and obtaining a clear picture of the mechanisms involved. As a matter of fact, the above considerations suggest an additional speculative assumption[15] concerning the shape and position of the minimum in the S_1 potential, which could be slightly shifted with respect to the case of St, possibly because of the molecular asymmetry. This could produce a decrease of the fraction of molecules decaying to the cis side from the twisted configuration.

In rigid matrix at low temperatures the internal rotation leading to isomerization, and likewise the IC, are inhibited. The reason for the low ϕ_F values of isomers 2 and 4 at 77 K is thus probably attributable to ISC which remains the only process competitive with fluorescence. In other words, we think that isomers 2 and 4 have higher ISC rate parameters compared to St and 3-StP but that the process becomes competitive with the emission only when k_R strongly decreases in rigid media. This hypothesis is confirmed by recent theoretical calculations which show isomers 2 and 4 to have k_{ISC} almost two orders of magnitude greater than 3-StP and St.[18]

α-Methylstyrylpyridines. The α-methylation causes a pronounced decrease of fluorescence in St and StP's which is accompanied, for St and 3-StP, by a noticeable decrease of ϕ_C. Moreover, like 2- and 4-StP and contrary to St and 3-StP, ϕ_C is independent of temperature in the range investigated (213–333 K) for all the α-CH_3 derivatives of St and StP's.

Another peculiar behavior of these hindered compounds, observed earlier by Fischer et al. for St,[6] is their capability of intramolecular rotation in high viscosity media. There is in fact competition between fluorescence and twisting in these compounds even in rigid matrix at 77 K. The photoisomerization quantum yields at 77 K (Table II) are of the order of 10% while the fluorescence quantum yields range from 13 to 42%. The possibility of rotation in the matrix is due to the different geometry assumed by the molecule owing to steric hindrance, the nonplanarity leading to a similar molecular volume for the two geometrical isomers.[6,20] While in the ground state the hindrance is relieved by twisting around the exocyclic single bond, in the excited state the repulsive energy produced by the crowding induces a twisting around the central α–α′ bond because of the decrease of the bond order on excitation.[23] This could favor the competition of radiationless processes, including the "horizontal" trans → perp process,[2a] with fluorescence thus explaining the decrease of ϕ_F compared to the unsubstituted molecules and the independence of ϕ_C on temperature for all the α derivatives under study.

It is interesting to recall that the results of sensitized experiments with triplet donors led to the conclusion that both trans and cis α-CH_3St can undergo nonvertical transitions to the T_1 state requiring less energy than the Franck–Condon vertical excitation. This hypothesis implies that excitation of these nonplanar flexible molecules can produce twisted geometric forms directly.[24]

The potential energy surfaces of both ground and excited states of the hindered compounds may differ substantially from those of St in the position of the energy minima as well as in the height of the rotation barrier around the α–α′ bond. As the Stokes shifts of the α-CH_3 derivatives do not seem to indicate too large a displacement between the S_1 and S_0 minima in the trans region, the energy barrier to rotation (practically absent) and the location of the minima in the region of the perpendicular configuration should (in addition to the relative position of (n,π*) and (π,π*) states) be the main factors responsible for the photophysical and photochemical behavior of the α-CH_3 substituted compounds. In particular, the IC of the twisted form to S_0 may occur on the left side of the ground state curve toward the trans configuration (see Figure 1).

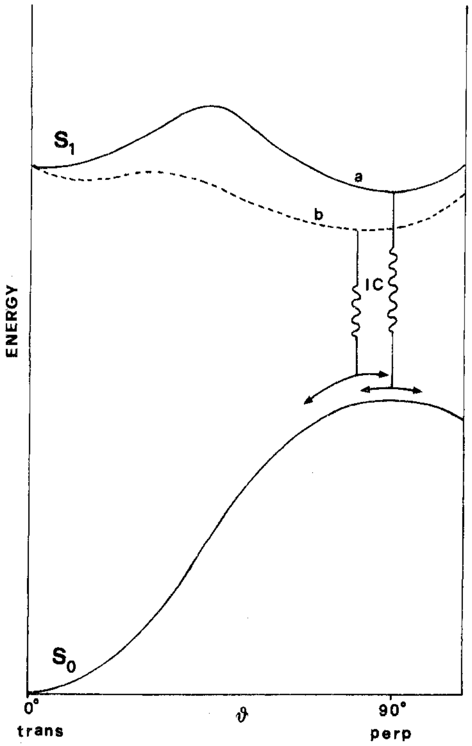

Figure 1. Schematic energy profiles for the twisting mode of the lowest excited state in stilbene (a) and hindered stilbenes (b).

For St and 3-StP, α substitution brings about a pronounced reduction in ϕ_C probably for this reason. On the other hand, the sketch foresees an increase of the backphotoreaction. It is worthwhile to note in this respect that the quantum yield for the cis → trans photoisomerization (ϕ_T) reported by Fischer et al.[6] for α-CH_3St in isohexane is higher than ϕ_C.

For the α-CH_3 derivatives of 2- and 4-StP, the ϕ_C values in *n*-hexane remain practically unchanged compared to the unsubstituted isomers. It should be noted, however, that, even if there is a high percentage of decrease in ϕ_F, the "recovered" quanta may be in any case too few to lead to a clear change of the photoreaction yield.

As to the emission yields at 77 K, the data in Table II show that α substitution markedly reduces the fluorescence of St and 3-StP while leaving ϕ_F of isomers 2 and 4 practically unchanged. On the basis of the conclusions reached for the unsubstituted compounds, it can be assumed that here again the α-CH_3-substituted 2-StP and 4-StP have higher ISC rate parameters. Probably, the easier pathway to the triplet manifold for the last two isomers explains why their reaction yield in glassy matrix is of the same order as for the other two α-CH_3 compounds which undergo the net ϕ_F decrease.

Solvent Effect. To obtain additional information on the competition between emission and internal rotation, the effect of other solvents was examined. Table V reports

TABLE V: Fluorescence Quantum Yields of Stilbene Analogues in Water-Ethanol 50/50 (v/v) and Glycerol at 298 K

trans isomers	water-ethanol	glycerol
St	0.021	0.20
2-StP	0.004	0.04
3-StP	0.031	0.16
4-StP	0.0016	0.014
α-CH_3St	$<6 \times 10^{-4}$	0.002
α-CH_3-2-StP	$<6 \times 10^{-4}$	0.0037
α-CH_3-3-StP	0.0018	0.014
α-CH_3-4-StP	$<6 \times 10^{-4}$	0.0013

the fluorescence quantum yields of the hindered compounds in a viscous solvent, glycerol, compared to those in 50/50 (v/v) water–ethanol (to compensate polar and protic effects). Similar data for the unsubstituted compounds are also reported.

On going from hydrocarbon solvent to water–ethanol, there is a decrease of ϕ_F for St and 3-StP and an increase for 2-StP. Taking into account that ϕ_C goes in the same direction, one can infer that the solvent affects mainly ϕ_{IC}. This can be due to a decrease in energy of the $^1B_u{}^*$ state (more sensitive to solvent than $^1A_g{}^*$),[25] which changes the profile of the S_1 potential as a function of ϑ. In the case of the aza compounds, an additional effect plays a role because of the increase in energy of the (n,π^*) states which favors fluorescence and photoreaction of isomer 2. It is not possible to estimate the effect on the α-CH_3 derivatives as ϕ_F remains too low in both solvents, except for α-CH_3-3-StP.

On going from water–ethanol to glycerol, there is a general increase of one order of magnitude in the fluorescence yield due to viscosity. Absorption spectra in glycerol indicate that the viscous solvent induces a negligible reduction of the fluorescence rate parameter, k_F. The main effect is probably a decrease in the rate constant for internal rotation, k_R. If this is the case, the increase of the singlet lifetime explains the increase of ϕ_F (see Table V). A parallel increase of ϕ_{ISC} should be expected which opens the way to isomerization via the triplet[25] so that the overall ϕ_C (singlet + triplet) could remain high in glycerol at room temperature. Literature data for St and α-CH_3St,[6] recently confirmed in this laboratory, indicate in fact that ϕ_C practically does not change on going from the inert solvent to glycerol. Reduction of isomerization in the singlet manifold due to the viscosity barrier is probably compensated by the population of the reactive triplet state induced by the viscous solvent.

Conclusions

The results of this work lead to some interesting conclusions on the competition between fluorescence and radiationless transitions in planar and nonplanar azastilbenes.

Considering IC from the planar trans form (at $\vartheta = 0°$) to be rather unlikely and including IC from twisted forms ($\vartheta > 0°$) in the "horizontal"[2a] rotational process, we can express the fluorescence quantum yield in general as $\phi_F = k_F/(k_F + k_{ISC} + k_R)$. For St and 3-StP in fluid medium, $k_R \gg k_F \gg k_{ISC}$ (k_{ISC} is relatively negligible), while in a rigid matrix, $k_F \gg k_{ISC}$ (k_R is negligible). Correspondingly, $\phi_F = 1$ at 77 K. For 2-StP and 4-StP in fluid medium, $k_R \gg k_F \simeq k_{ISC}$ (k_{ISC} is nonnegligible), while in a rigid matrix, $k_F \simeq k_{ISC}$ (only k_R is negligible). Correspondingly, $\phi_F = k_F/(k_F + k_{ISC}) < 1$ at 77 K.

The competition between the deactivation processes plays a similar role in the photoisomerization whose yield depends on the decay fraction and becomes zero in a rigid matrix.

The α-CH_3 derivatives behave in a similar manner. The main difference is a somewhat smaller value for ϕ_C and a nonnegligible k_R in glassy medium.

These results confirm the importance of the shape of the potential energy surfaces as a function of twisting in the singlet manifold in determining the rate of geometrical photoconversion of azastilbenes. Obviously, lifetime measurements in fluid and viscous solvent would help in the interpretation of their behavior but unfortunately they are in the picosecond region, below the resolution limit of our apparatus. We are now extending the measurements to other solvents, including plastics, and to lower temperatures to gain further insight in the photoreaction mechanism.

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