

## 3-STYRYLQUINOLINE CONFORMERS: A PHOTOPHYSICAL AND PHOTOCHEMICAL STUDY†

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### Summary

The emission spectrum of a  $10^{-6}$  M cyclohexane solution of *trans*-3-styrylquinoline varies with the excitation wavelength. Fluorescence excitation spectra at room temperature and at 77 K indicate the presence of two emitting species which are assumed to be conformational isomers arising from rotation about the single bond linking the styryl part of the molecule to the quinoline ring. The dependence of the photophysical and photochemical properties of *trans*-3-styrylquinoline in various solvents on the excitation wavelength are reported. The influence of pH on the composition of the conformers and the dependence on the excitation wavelength of the percentage of molecules which attain the prototropic equilibrium in the excited state were studied.

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### 1. Introduction

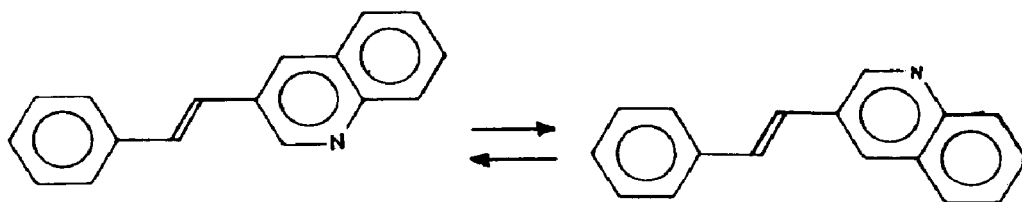
Multiple fluorescence emission of molecules in dilute solutions is a well-established phenomenon. Processes which lead to dual emission include the following: (a) the establishment of a prototropic equilibrium in the excited singlet state for aromatic molecules which contain an acidic or a basic group [1]; (b) intramolecular excimer formation for diarylalkanes, particularly 1,3-diarylalkanes, and vinyl polymers with an aromatic substituent [2]; (c) intramolecular charge transfer processes in organic molecules in which both electron-donating and electron-withdrawing groups are present simultaneously (*e.g.* in *p*-dimethylaminobenzonitrile) [3].

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More recently a number of workers have reported that another class of compounds, the *trans*-1,2-diarylethylenes, show multiple emission in solution [4 - 8]. The evidence is both spectroscopic (the fluorescence emission spectrum varies with the wavelength of the exciting light) and kinetic (the fluorescence decay has two components with different lifetimes and the fluorescence quantum yield depends on the excitation wavelength). These results have been ascribed to the existence in solution of at least two conformational isomers of the *trans*-1,2-diarylethylene. The conformers result from a rotation around the quasi-single bond between the aryl groups and the ethylenic carbon. These almost planar and nearly isoenergetic conformers have different, but overlapping, absorption and fluorescence spectra and different fluorescence parameters. Under certain conditions and especially at low temperatures [9] it is possible to excite one of the conformers selectively by irradiating at its absorption edge and thus to obtain information on a single species.

In this paper the wavelength dependences of the emission properties and of the *trans*  $\rightarrow$  *cis* photoisomerization yields of 3-styrylquinoline (3-StQ), a molecule belonging to this new class of compounds, are reported. The study was carried out in various solvents and in aqueous solution at various pH values with the aim of obtaining information on the influence of the solvent polarity and of pH on the conformational equilibrium



Moreover the  $pK_a$  of the first excited singlet state of this molecule was obtained by fluorometric titration and the influence of the excitation wavelength on the prototropic equilibrium in the excited state was examined.

## 2. Experimental details

The compound studied had been prepared previously [10]; its purity was checked using gas chromatographic analysis. Cyclohexane (Carlo Erba, RS grade) was used as received. Acetonitrile (Carlo Erba, RP grade) was distilled over  $P_2O_5$  and again from anhydrous  $K_2CO_3$ . 3-methylpentane (Carlo Erba, RP grade) was shaken with small portions of oleum and then with concentrated  $H_2SO_4$  until the acid layer remained colourless. It was then washed with water, aqueous 10%  $Na_2CO_3$  and water to neutrality, dried with  $MgSO_4$  and distilled over sodium.  $CH_3OH$ ,  $C_2H_5OH$  and ethylene glycol (all Carlo Erba products) were used as received. Britton buffers ( $\mu = 1$  by  $NaClO_4$  which does not quench the fluorescence) and 1 N KOH solutions,

both in 10 vol.% ethanol, were used for experiments in aqueous solutions. Fluorescence and photoisomerization quantum yields were measured at room temperature ( $20 \pm 2^\circ\text{C}$ ). The fluorescence measurements were performed using a Perkin-Elmer MPF 44A spectrofluorometer equipped with an accessory for spectra correction. Fluorescence quantum yields were determined using cyclohexane solutions of 9,10-diphenylanthracene ( $\phi_f = 1$ ) [11] and/or 2-(1-naphthyl)-5-phenyl-1,3,4-oxadiazole ( $\phi_f = 0.7$ ) [11] as standards. The  $\phi_f$  values obtained with the two standards are in good agreement with each other. No correction for the differences in refractive index was made [12]. The maximum optical density values of the solution used for  $\phi_f$  and the determination of the corrected excitation spectra was less than 0.05 in a cell 1 cm thick. A fixed value of 2.5 nm was used for both the excitation and emission slits. The  $\phi_f$  values reported are the averages of three independent runs; the mean deviation did not exceed 5%. Fluorescence lifetimes were measured using a single-photon counting apparatus obtained from Applied Photophysics.

The photoisomerization quantum yields were determined in air-saturated solutions in conditions of total absorption of the incident light ( $c = 3 \times 10^{-4}$  M; cell path length, 1 or 4 cm). For experiments in aqueous solvents the ethanol content was 15 vol.% and the ionic strength was 0.1 to avoid the precipitation of 3-StQ. The light source was a stabilized high pressure xenon arc (Osram XBO 150 W) from which the exciting wavelength was isolated using narrow band interference filters (Ealing). The intensity of the incident light was determined by ferrioxalate actinometry [13]. Irradiations were carried out up to about 10% conversion to ensure that the contribution of the back reaction was negligible (the *cis* percentage at the photostationary state is 40% at every excitation wavelength). The conversion percentages were determined by UV spectrophotometry in the region 300 - 340 nm after suitable dilution of the irradiated solutions. A double-beam Perkin-Elmer-Coleman spectrophotometer (model 572) was used. The  $\phi_c$  values reported are the averages of from eight to ten independent runs; the mean deviation was 7%.

### 3. Results and discussion

#### 3.1. Spectral properties

The absorption spectrum of *trans*-3-StQ in cyclohexane solution is reported in Fig. 1. The spectrum closely resembles that of the parent hydrocarbon  $\beta$ -styrylnaphthalene. In the spectrum of the latter compound, benzenic, ethylenic and naphthalenic character has been assigned to the transitions centred at 280, 315 and 350 nm respectively [14]. Given the strong similarity between the spectra of the two molecules, a similar assignment is reasonable for the 3-StQ transitions. No evidence was obtained for the quinolinic  $n,\pi^*$  transition, which is presumably masked by the much more intense  $\pi,\pi^*$  transition. It is worth remembering that both complete

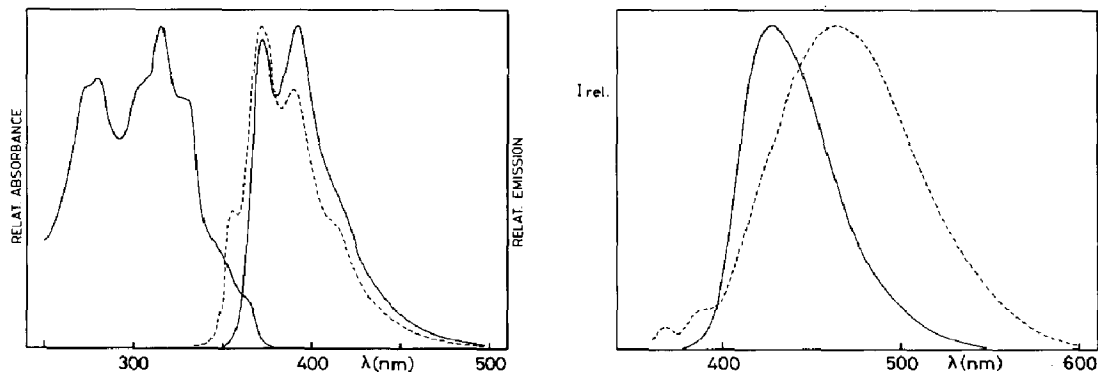


Fig. 1. Absorption and fluorescence emission spectra of *trans*-3-StQ in a cyclohexane solution: ---,  $\lambda_{\text{exc}} = 315 \text{ nm}$ ; —,  $\lambda_{\text{exc}} = 350 \text{ nm}$ .

Fig. 2. Emission spectra of *trans*-3-StQ at 77 K: ---, 3-methylpentane glassy solution; —, polycrystalline compound.

and intermediate neglect of differential overlap/spectroscopic calculations [15, 16] for styrylpyridines, the aza analogues of stilbene, have predicted that the lowest  $n, \pi^*$  singlet state of these molecules, lies at an energy about 0.3 - 0.5 eV higher than that of the  $\pi, \pi^*$  ethylenic-type singlet state.

When *trans*-3-StQ is excited at the 315 nm absorption maximum of the molecule it shows a fluorescence spectrum with peaks at 357, 372 and 393 nm and a shoulder at about 415 nm. Changing the excitation wavelength produces only a slight variation in the ratio of the height of the most intense peak at 372 nm to that of the peak at 393 nm and to the shoulder at 415 nm, whereas large variations are observed for the ratio  $I_{372}/I_{357}$ . Excitation at the long wavelength edge of the absorption (345 - 365 nm) results in an emission spectrum in which the peak at 357 nm is absent. The fluorescence spectra obtained by excitation at 315 nm (the excitation wavelength most favourable for the observation of the 357 nm fluorescence peak) and 350 nm are shown in Fig. 1.

The emission spectra obtained in a rigid matrix at 77 K are usually much sharper, which may be useful for the separation of the emission of the two species. Surprisingly, a 3-methylpentane solution ( $c = 1.5 \times 10^{-6} \text{ M}$ ) cooled to 77 K by immersion in liquid nitrogen shows a broad structureless emission with a maximum at about 460 nm (Fig. 2). The spectrum obtained is similar to that of the polycrystalline compound which is included for comparison. A bathochromic shift of about 30 nm, however, is observable in the emission of glassy solutions with respect to the spectrum of polycrystalline samples. This similarity suggests that precipitation or some form of aggregation is responsible for the emission in pure glassy 3-methylpentane. Aggregation phenomena have been observed for similar compounds (e.g. 1,2-di(2-naphthyl)ethylene) in poor solvents at low temperatures [17]. Sharp spectra have been obtained at 77 K in 3-methylpentane containing 2 vol.% 2-methyltetrahydrofuran. However, there was no substantial improvement in resolution compared with the emission spectrum obtained in

the same solvent at room temperature. The emission spectrum has three maxima at 365 - 366, 386 and 405 nm and a shoulder at about 430 nm whose relative intensity varies with the excitation wavelength. The spectra obtained on excitation at 290 and 310 nm (Fig. 3) illustrate the variation observed. Freezing the solutions causes a hypsochromic shift of the bands observed in fluid solutions which prevents the observation of the band with a maximum at 357 nm which is present at room temperature for  $\lambda_{\text{exc}} < 330$  nm.

More detailed information on the spectroscopic properties of the two conformers has been obtained from fluorescence excitation spectra in both a fluid solution at room temperature and a glassy solvent at 77 K. The excitation spectra in cyclohexane solutions at room temperature were monitored at 357, 375 and 410 nm. The spectra are shown in Fig. 4; none of them can be superimposed on the absorption spectrum. It can be seen that the long wavelength fluorescence has an excitation spectrum which is richer in the naphthalenic type of transition than is the excitation spectrum of the fluorescence peak at 357 nm. The same excitation spectrum was obtained on monitoring the fluorescence at 410 nm and at 440 nm, *i.e.* in the tail of the emission band. If it is assumed that the fluorescence maximum at 357 nm is due to the emission of a single component and that the fluorescence tail is constituted from the emission of the second rotational isomer only, fluorescence excitation spectra A and C of Fig. 4 represent the absorption spectra of the two conformers. The absorption spectra of the two conformational isomers of *trans*-1-phenyl-2(2-naphthyl)ethylene were obtained by exploiting the fact that the two isomers have different fluorescence lifetimes [6]. Unfortunately, the above method cannot be applied to 3-StQ because the fluorescence decay in cyclohexane at room temperature was found to be monoexponential with a lifetime of 1.8 ns ( $\chi^2 = 1.10$  with weighted residuals regularly distributed along the time axis). The monoexponential decay could

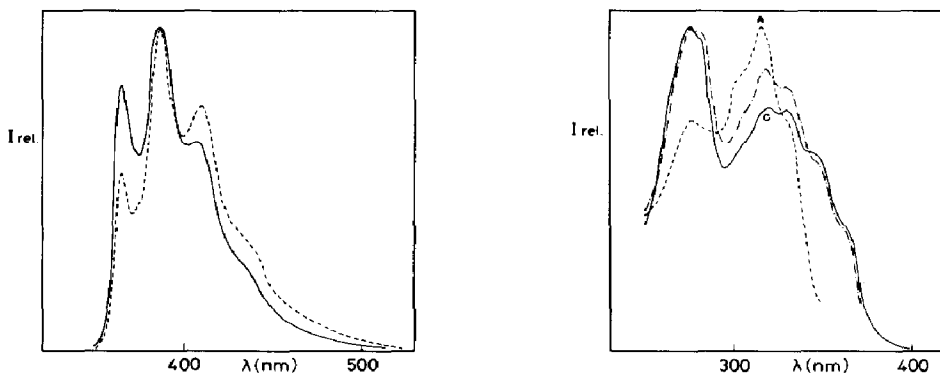


Fig. 3. Emission spectra of *trans*-3-StQ in a 3-methylpentane solution containing 2 vol.% 2-methyltetrahydrofuran at 77 K: —,  $\lambda_{\text{exc}} = 290$  nm; ---,  $\lambda_{\text{exc}} = 310$  nm.

Fig. 4. Room temperature excitation spectra of *trans*-3-StQ in cyclohexane solution at various fluorescence analysis wavelengths: ---, 357 nm; - · -, 375 nm; —, 410 nm. All the spectra are normalized to the excitation maximum.

be explained if one conformer had a very short lifetime ( $\tau < 0.2$  ns) which was less than the resolution time of our fluorometer. In fact two exponential decays with lifetimes of 1.7 ns and 5.7 ns respectively were obtained at 77 K in 3-methylpentane containing 5 vol.% 2-methyltetrahydrofuran. Alternatively the two conformers could have very similar lifetimes at room temperature, the lifetime of one conformer being temperature independent ( $\tau \approx 1.7$  ns) and that of the other showing the usual increase with decreasing temperature observed for stilbene-like molecules [18].

Fluorescence excitation spectra at 77 K are better resolved than those at room temperature and show some unusual properties when recorded at various emission wavelengths. On increasing the wavelength of the fluorescence analysis from 360 to 440 nm the following behaviour is observed.

(a) The intensities of the bands peaked at 281 and 292 nm increase progressively (the excitation spectra obtained with  $\lambda_{em}$  values of 365 and 408 nm (Fig. 5) illustrate the type of behaviour observed).

(b) The band width of the peaks in the region 300 - 340 nm broadens.

(c) The excitation peak at 338 nm, which is observed on analysing the emission at 360 - 365 nm, is gradually replaced by a peak at 333 nm when the emission analysis wavelength increases.

Unfortunately, observation of the excitation spectra in the region 350 - 400 nm for the short wavelength of the fluorescence emission is prevented by the strong intensity of the scattered light; therefore possible differences with respect to the long wavelength emission in this spectral region cannot be observed.

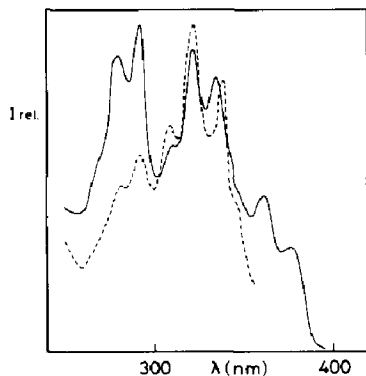


Fig. 5. Fluorescence excitation spectra of *trans*-3-StQ in a glassy solution of 3-methylpentane containing 5 vol.% 2-methyltetrahydrofuran at 77 K: ---,  $\lambda_{em} = 365$  nm; —,  $\lambda_{em} = 408$  nm. The spectra are normalized to the excitation maximum.

### 3.2. Quantum yields

The influence of the excitation wavelength on the shapes of the fluorescence spectra is reflected by the  $\phi_f$  values obtained for various  $\lambda_{exc}$ . These values, together with the values of the *trans*  $\rightarrow$  *cis* photoisomerization quantum yield  $\phi_c$  in air-saturated cyclohexane solutions, are reported in Table 1. The removal of oxygen by bubbling pure nitrogen through the solution

TABLE 1

Wavelength dependence of the fluorescence quantum yield  $\phi_f$  and the *trans*  $\rightarrow$  *cis* photoisomerization quantum yield  $\phi_c$  of *trans*-3-styrylquinoline in cyclohexane and acetonitrile

$\lambda$ (nm)	Cyclohexane		Acetonitrile	
	$\phi_f$	$\phi_c$	$\phi_f$	$\phi_c$
240	0.32		0.42	
250	0.30		0.38	
255	0.31 <sub>5</sub>	0.25	0.41 <sub>5</sub>	0.25
260	0.35		0.40 <sub>5</sub>	
270	0.35 <sub>5</sub>		0.41	
280	0.36	0.37	0.42 <sub>5</sub>	0.21
290	0.29		0.40 <sub>5</sub>	
300	0.26		0.35 <sub>5</sub>	
310	0.25 <sub>5</sub>		0.35 <sub>5</sub>	
315	0.25	0.49	0.34	0.26 <sub>5</sub>
320	0.25 <sub>5</sub>		0.38	
330	0.28 <sub>5</sub>		0.38 <sub>5</sub>	
340	0.39 <sub>5</sub>		0.51 <sub>5</sub>	
345	0.46	0.30 <sub>5</sub>	0.61	0.19 <sub>5</sub>
350	0.53		0.65	
360	0.55		0.64	
365	0.58 <sub>5</sub>	0.23	0.68 <sub>5</sub>	0.19 <sub>5</sub>

causes a small increase in  $\phi_f$  (about 10%) together with a decrease in  $\phi_c$ . This is in agreement with the short ( $\tau = 1.8$  ns) fluorescence lifetime of 3-StQ in cyclohexane solution at room temperature. There is almost no variation with  $\lambda_{\text{exc}}$ . As can be seen from the data in Table 1, the fluorescence and photoisomerization yields are complementary: the minimum value of  $\phi_f$  (0.25 at  $\lambda_{\text{exc}} = 315$  nm) corresponds to a maximum value for  $\phi_c$  (0.49). Excitation at long wavelengths leads to high fluorescence yields and low photoisomerization yields. It can therefore be concluded that the potential energy surfaces of the two electronically excited conformers have rather different properties so that one of the excited conformers deactivates mainly through a photo-physical process (fluorescence emission) and the other deactivates mainly through a photochemical channel (the geometrical *trans*  $\rightarrow$  *cis* isomerization). It can be argued from the fluorescence excitation spectra and from the values of  $\phi_f$  and  $\phi_c$  that the fluorescence excitation spectrum A (see Fig. 4) is (or is very similar to) the absorption spectrum of the conformer which isomerizes with high efficiency and that the fluorescence excitation spectrum C is (or is very similar to) the absorption spectrum of the conformer which fluoresces with high efficiency.

### 3.3. Solvent effect

The absorption spectrum of 3-StQ in polar solvents (acetonitrile, methanol and ethanol) undergoes only a very minor bathochromic shift with respect to the spectrum in cyclohexane. The most important modification in

TABLE 2

Fluorescence maximum  $\lambda_{\max}$  for *trans*-3-styrylquinoline in various solvents obtained at various excitation wavelengths

$\lambda_{\text{exc}}$ (nm)	Fluorescence maximum (nm) in the following solvents			
	Cyclohexane	Acetonitrile	Ethanol	Methanol
280	372 - 373	395	405	402 - 403
315	372 - 373	390	395	400
340	372 - 373	398 - 400	400	404
370	372 - 373	400	405	408 - 409

these solvents is the loss of all vibrational structure in the region 340 - 370 nm. The photophysical and photochemical properties of 3-StQ, however, are strongly modified. No vibrational structure is detectable in fluorescence emission spectra and the maximum of the fluorescence band undergoes a bathochromic shift with respect to its value in cyclohexane solution. When  $\lambda_{\text{exc}} = 315$  nm,  $\lambda_{\max}$  is 390 nm, 395 nm and 400 nm in acetonitrile, ethanol and methanol respectively. Moreover, the emission maximum varies with the excitation wavelength. The values of the emission maxima  $\lambda_{\max}$  of 3-StQ in the above solvents at various excitation wavelengths are given in Table 2. The variation in fluorescence maximum  $\lambda_{\max}$  with the excitation wavelength can reasonably be ascribed to the variation in the contributions of the two conformers with  $\lambda_{\text{exc}}$ . Hydrogen bonding phenomena probably contribute to the shifts in the fluorescence maxima. In fact the red shift of the emission in methanol with respect to the fluorescence in acetonitrile is not justified by the different values of the dielectric constants  $\epsilon$  of the two solvents (37.5 and 32.7 in acetonitrile and methanol respectively).

The fluorescence excitation spectra in the above three solvents at room temperature and in a 50vol.%methanol-50vol.%ethanol glass at 77 K have features very similar to those observed in non-polar solvents that have been described already.

The  $\phi_f$  and  $\phi_c$  values obtained in acetonitrile solution for various values of  $\lambda_{\text{exc}}$  are reported in Table 1. As in cyclohexane solution, both these parameters vary with the excitation wavelength. However, the variation is more sensitive for the fluorescence parameter than for the photochemical parameter. Comparison with the corresponding values obtained in cyclohexane shows that there is a general increase in  $\phi_f$  and a decrease in  $\phi_c$ . It is impossible to determine whether these variations with respect to the non-polar medium are due to a solvent-induced enrichment of the 3-StQ solution in the conformer with a high fluorescence quantum yield or to a modification of the excited state potential energy surface of the conformer which has a low fluorescence quantum yield in cyclohexane such that the probability of radiative deactivation is increased in the polar solvent.



### 3.4. pH effects

No appreciable variation in the absorption spectrum of aqueous 3-StQ solutions containing 1 N KOH with respect to those obtained in polar organic solvents was observed. On protonation, the spectrum broadens and the band centred at 345 nm shifts to the red as shown in Fig. 6. The fluorescence spectrum shows similar shifts, with the maximum in the basic solution being at 415 nm and that in the acid solution being at 510 nm (Fig. 7). The fluorescence characteristics of KOH solutions of 3-StQ parallel those of polar solutions. The position of the fluorescence maximum varies from 412 to 420 nm depending on the excitation wavelength. The fluorescence excitation spectra at room temperature and in a glassy 50vol.%ethylene glycol-50vol.%KOH (1 N) matrix are dependent on the fluorescence analysis wavelength, e.g. in the excitation spectra recorded with a short fluorescence wavelength (375 nm) the most intense band peaks at 317 nm and in the spectra recorded with a long fluorescence wavelength (450 nm) the most intense band peaks at 280 nm and furthermore the naphthalenic-type transition zone (340 - 370 nm) is more intense than the excitation spectrum obtained by analysing the fluorescence at short wavelengths. The same phenomena are observed at 77 K; naturally the bands observed are sharper and show a more resolved vibrational structure relative to the spectra obtained at room temperature. The fluorescence and photoisomerization quantum yields in 1 N KOH are collected in Table 3. These quantities also show a wavelength dependence in this solvent, and the maximum value of  $\phi_c$  is found at 315 nm where  $\phi_f$  is low.

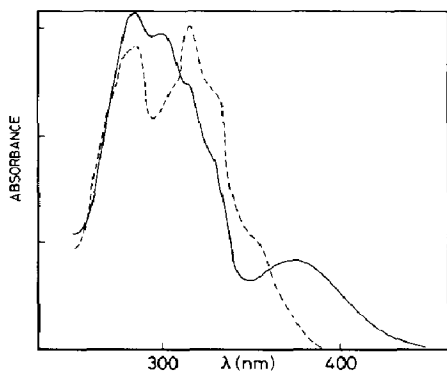


Fig. 6. Room temperature absorption spectra of *trans*-3-StQ in an aqueous solution containing 10 vol.% methanol: —, 0.1 N HClO<sub>4</sub>; - - -, 1 N KOH.

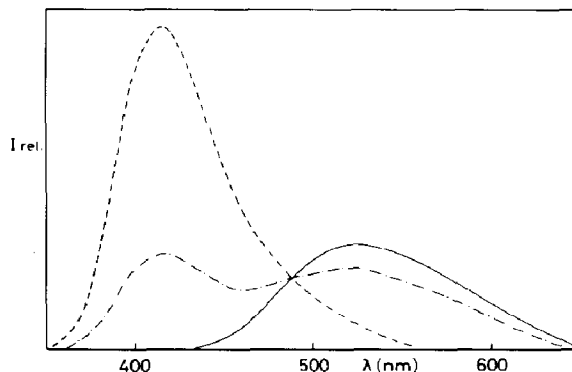


Fig. 7. Room temperature fluorescence emission spectra of *trans*-3-StQ in aqueous solutions containing 10 vol.% ethanol: —, 0.1 N HClO<sub>4</sub>; - · -, Britton buffer, pH 8; - - -, 1 N KOH.

In a highly acidic medium the shape and the maximum of the fluorescence spectrum showed no dependence on the excitation wavelength. Excitation spectra recorded at various emission wavelengths are almost identical and can be superimposed on the absorption spectrum. However, the fluorescence excitation spectra in a glassy 50vol.%ethylene glycol-50vol.%HClO<sub>4</sub>

TABLE 3

Wavelength dependence of the quantum yield of fluorescence  $\phi_f$  and the quantum yield of *trans*  $\rightarrow$  *cis* photoisomerization  $\phi_c$  of *trans*-3-styrylquinoline in 0.1 N HClO<sub>4</sub> and in 1 N KOH aqueous solutions containing 15 vol.% ethanol

$\lambda$ (nm)	0.1 N HClO <sub>4</sub>		1 N KOH	
	$\phi_f$	$\phi_c$	$\phi_f$	$\phi_c$
240	0.20 <sub>5</sub>		0.44	
250	0.21 <sub>5</sub>		0.44	
255	0.22 <sub>5</sub>		0.46	0.16
260	0.26		0.47	
270	0.23		0.44 <sub>5</sub>	
280	0.20 <sub>5</sub>	0.07	0.44	0.12 <sub>5</sub>
290	0.19 <sub>5</sub>		0.42	
300	0.21		0.39 <sub>5</sub>	
310	0.21 <sub>5</sub>		0.40	
315	0.22	0.09	0.39	0.18 <sub>5</sub>
320	0.19		0.39 <sub>5</sub>	
330	0.19		0.41 <sub>5</sub>	
340	0.19 <sub>5</sub>		0.48 <sub>5</sub>	
345	0.21 <sub>5</sub>	0.11 <sub>5</sub>	0.51	0.14 <sub>5</sub>
350	0.24		0.57 <sub>5</sub>	
360	0.23		0.56 <sub>5</sub>	
365	0.23	0.09	0.53	
370	0.26		0.57 <sub>5</sub>	
380	0.24	0.08		
390	0.26			
400	0.26 <sub>5</sub>			

(1 N) matrix at 77 K suggest the simultaneous presence of two emitting species in the acidic medium (Fig. 8).

The situation in a buffered medium at pH 8 is quite complicated. *trans*-3-StQ has a ground state  $pK_a$  of 4.8, as determined from absorption *versus* pH curves. As already found for some azastilbenes [19], azaphenanthrenes [20] and naphthylpyridylethylenes [21], the basicity of 3-StQ increases markedly in the first excited singlet state. Therefore the emission spectrum of 3-StQ has two maxima at pH 8: the first, at 417 nm, is due to the emission from the free base and the second, at 510 nm, is characteristic of the cation. The intensities of the peaks remain almost unchanged in the pH range 7 - 11.5. Above pH 11.5, the intensity of the 417 nm band increases markedly while the 510 nm band is correspondingly quenched. In 1 N KOH the band corresponding to the free base reaches its maximum intensity, while the band corresponding to the cation has completely disappeared. The presence of the partial cation emission at  $pH \gg pK_a$  indicates that some of the molecules have attained the prototropic equilibrium pertaining to the singlet excited state.

The absorption spectra of 3-StQ and its conjugate acid have isosbestic points at 270, 310 and 357 nm, and hence the ground and excited state

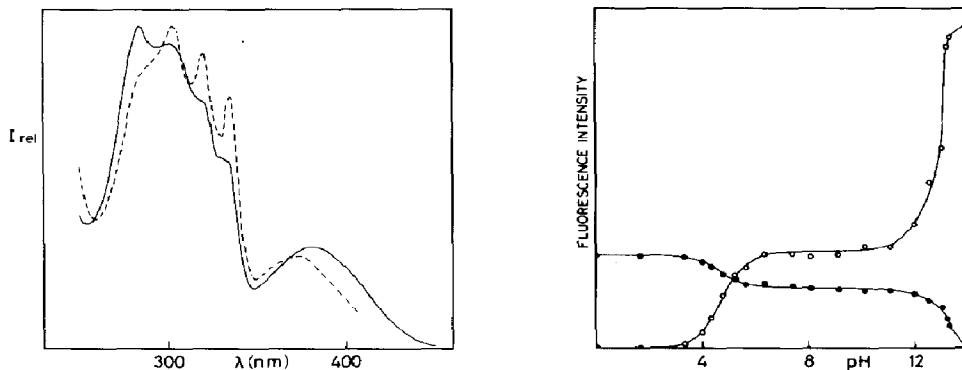


Fig. 8. Fluorescence excitation spectra of *trans*-3-StQ in a glassy 50vol.%ethylene glycol-50vol.%HClO<sub>4</sub> (1 N) matrix at 77 K: —,  $\lambda_{em} = 415$  nm; - - -,  $\lambda_{em} = 490$  nm.

Fig. 9. Fluorometric titration curve of *trans*-3-StQ: ●, measurements on the band corresponding to the protonated form at 550 nm; ○, measurements on the band corresponding to the basic form at 420 nm. The excitation was performed at the isosbestic point (310 nm).

ionization constants can be determined by direct fluorometric titration. The fluorescence *versus* pH curves for the emission at 420 nm and 550 nm, where there is effectively no contribution from the acidic form and the basic form respectively, obtained by exciting at 310 nm are shown in Fig. 9. A  $pK_a^*$  value of 12.7 is obtained from these curves. The values of  $I_a/I_a^0$  and  $1 - I_b/I_b^0$  calculated from these curves, where  $I_a$  and  $I_b$  are the intensities of the acid and the base emissions at pH 9 and  $I_a^0$  and  $I_b^0$  are the limiting intensities of the acid and the basic forms of 3-StQ, give the fraction of the excited molecules equilibrated with the proton. This value, which strongly depends on the percentage of alcohol in the solution, is 65.6% for excitation at 270 and 357 nm and 71% for excitation at 310 nm of solutions containing 2 vol.% ethanol. No appreciable variation in  $pK_a$  and  $pK_a^*$  was observed on varying  $\lambda_{exc}$ . Therefore the presence of the two conformers in solution is reflected by the different percentages of molecules attaining equilibrium in the excited state. However, it is difficult to envisage how two conformers arising from rotation about the single bond in an extended aromatic system like 3-StQ would have acid properties so different as to be manifested as a different position of the inflection point on the fluorometric titration curves.

A more complete evaluation of the influence of  $\lambda_{exc}$  on the excited state acid-base equilibrium and on the fluorescence properties of 3-StQ in Britton buffer solutions containing 10 vol.% ethanol is obtained from the data given in Table 4. The total fluorescence quantum yield values for various excitation wavelengths are given in the second column: the values show the dependence on  $\lambda_{exc}$  described earlier. The third and fourth columns give the quantum yields of the basic and acidic parts of the emission (the percentage of the total emission due to the acidic component is shown in parentheses). These results were obtained as follows. The fluorescence spectra in the Britton buffer at pH 8 and in 1 N KOH were normalized at the

TABLE 4

Wavelength dependence of fluorescence parameters of *trans*-3-styrylquinoline in Britton buffer solutions (pH 8) containing 10 vol.% ethanol ( $\mu = 1$  by  $\text{NaClO}_4$ )

$\lambda_{\text{exc}}$	$\phi_{\text{tot}}$	$\phi_{\text{b}}$	$\phi_{\text{a}} (\phi_{\text{a}}/\phi_{\text{tot}})$	$\phi_{\text{b}}/\phi_{\text{b}}^0$	$1 - \phi_{\text{b}}/\phi_{\text{b}}^0$	$(\phi_{\text{a}}^0)_{\text{calc}}$
240	0.35 <sub>5</sub>	0.18 <sub>5</sub>	0.17 (0.48)	0.42	0.58	0.29 <sub>5</sub>
250	0.35	0.17 <sub>5</sub>	0.17 <sub>5</sub> (0.50)	0.40	0.60	0.29
255	0.36	0.18 <sub>5</sub>	0.17 <sub>5</sub> (0.48 <sub>5</sub> )	0.40	0.60	0.29
260	0.37	0.20	0.17 (0.46)	0.42 <sub>5</sub>	0.57 <sub>5</sub>	0.29 <sub>5</sub>
270	0.33	0.17	0.16 (0.48 <sub>5</sub> )	0.38	0.62	0.26
280	0.34 <sub>5</sub>	0.18	0.16 <sub>5</sub> (0.48)	0.41	0.59	0.28
290	0.32	0.16	0.16 (0.50)	0.38	0.62	0.26
300	0.28 <sub>5</sub>	0.14	0.14 <sub>5</sub> (0.51)	0.35 <sub>5</sub>	0.64 <sub>5</sub>	0.22 <sub>5</sub>
310	0.29 <sub>5</sub>	0.14	0.15 <sub>5</sub> (0.52 <sub>5</sub> )	0.35	0.65	0.24
315	0.29	0.14	0.15 (0.52)	0.36	0.64	0.23 <sub>5</sub>
320	0.29 <sub>5</sub>	0.14 <sub>5</sub>	0.15 (0.51)	0.37	0.63	0.24
330	0.31	0.15 <sub>5</sub>	0.15 <sub>5</sub> (0.50)	0.37 <sub>5</sub>	0.62 <sub>5</sub>	0.25
340	0.40	0.21	0.19 (0.47 <sub>5</sub> )	0.43 <sub>5</sub>	0.56 <sub>5</sub>	0.33 <sub>5</sub>
345	0.43	0.23	0.20 (0.46 <sub>5</sub> )	0.45	0.55	0.36 <sub>5</sub>
350	0.50	0.27 <sub>5</sub>	0.22 <sub>5</sub> (0.45)	0.48	0.52	0.43
360	0.47 <sub>5</sub>	0.27	0.20 <sub>5</sub> (0.43 <sub>5</sub> )	0.48	0.52	0.39 <sub>5</sub>
365	0.48	0.27	0.21 (0.44)	0.51	0.49	0.43
370	0.53	0.30	0.23 (0.43 <sub>5</sub> )	0.52	0.48	0.48

emission maximum of the base (at this wavelength the acidic form does not emit) for every excitation wavelength. The area under the curve obtained in KOH was then subtracted from the area of the total fluorescence at pH 8 and the residual emission was assigned to the acidic component. The values given in the fifth column represent the fraction of the free base present at the prototropic equilibrium in the excited state. The complements to each of the values reported in the fifth column, *i.e.* the fractions of molecules present in the cationic form, are reported in the sixth column. The values in the seventh column are obtained by dividing the values in the fourth column by the corresponding value in the sixth column; they represent the values of  $\phi_{\text{f}}$  for the protonated form which would be obtained if the prototropic equilibrium in the excited state were fully attained. These values should correspond to the values of  $\phi_{\text{f}}$  for 3-StQH<sup>+</sup> reported in Table 3 if the same species were present in solution. However, they are generally higher than those of Table 3, in particular those obtained at long excitation wavelengths. It must therefore be concluded that the conformer composition in the Britton buffer is different from that in the strongly acidic medium. In particular, the less fluorescent conformer is more abundant at acidic pH values.

#### 4. Conclusion

The photochemical and photophysical properties of *trans*-3-StQ in solution are due to the presence of two conformers in equilibrium. These properties vary with the polarity of the solvent and its ability to participate in

hydrogen bonding. It is not clear at present whether these variations are due to some influence on the conformer composition or to a modification of the deactivation parameters of the excited state of the rotational isomers. It appears that the acidic medium favours enrichment of the mixture by the poorly fluorescent isomer.

Distinct fluorescence excitation spectra have been obtained by analysing the emission at long and short wavelengths. The spectra obtained are probably very similar to the true absorption spectra of the two conformers. In any case the determination of distinct excitation spectra of 3-StQ strongly supports the conclusion of Fischer and coworkers [9, 17] that the dependence of the emission behaviour of some *trans*-diarylethylenes on the excitation wavelength is due to conformers already present in solution and not to conformational changes occurring in the excited state.

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### References

- 1 S. Schulman, *Fluorescence and Phosphorescence Spectroscopy: Physicochemical Principles and Practice*, Pergamon, Oxford, 1977, Chap. 2, and references cited therein.
- 2 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, 1970, Chap. 7.
- 3 Z. R. Grabowski, K. Rotkiewicz, A. Siemiarz, D. J. Cowley and W. Bauman, *Nouv. J. Chim.*, **3** (1979) 443.
- 4 Yu B. Scheck, N. P. Kovalenko and M. V. Alfimov, *J. Lumin.*, **15** (1977) 157.
- 5 E. Fischer, *J. Photochem.*, **17** (1981) 331, and references cited therein.
- 6 J. B. Birks, G. Bartocci, G. G. Aloisi, S. Dellonte and F. Barigelletti, *Chem. Phys.*, **51** (1980) 113.
- 7 K. P. Ghiggino, *J. Photochem.*, **12** (1980) 173.
- 8 G. Bartocci and U. Mazzucato, *J. Lumin.*, **27** (1982) 163.
- 9 E. Haas, G. Fischer and E. Fischer, *J. Phys. Chem.*, **82** (1978) 1638.
- 10 G. Gennari, G. Cauzzo and G. Galiazzo, *J. Photochem.*, **5** (1976) 409.  
G. Gennari, G. Cauzzo and G. Galiazzo, *J. Phys. Chem.*, **81** (1977) 1551.
- 11 I. Beriman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York, 1965, pp. 130, 158.
- 12 F. J. Busselle, N. D. Haig and C. Lewis, *Chem. Phys. Lett.*, **72** (1980) 533.
- 13 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235** (1956) 18.
- 14 G. Wettermark, L. Tegnér and O. Martensson, *Ark. Kemi*, **30** (1968) 185.
- 15 G. Di Stefano, U. Mazzucato, A. Modelli, S. Pignataro and G. Orlandi, *J. Chem. Soc., Faraday Trans. II*, **71** (1975) 1583.
- 16 G. Orlandi, G. Poggi and G. Marconi, *J. Chem. Soc., Faraday Trans. II*, **76** (1980) 581.
- 17 E. Fischer, *J. Phys. Chem.*, **77** (1973) 859; **84** (1980) 403.
- 18 U. Mazzucato, *Pure Appl. Chem.*, **54** (1982) 1705.
- 19 G. Favaro, U. Mazzucato and F. Masetti, *J. Phys. Chem.*, **77** (1973) 601.
- 20 G. Gennari, G. Cauzzo and G. Galiazzo, *Gazz. Chim. Ital.*, **104** (1974) 535.
- 21 G. Favaro, F. Masetti, U. Mazzucato and P. Bortolus, *J. Phys. Chem.*, **79** (1975) 2785.