SOLVENT EFFECTS ON THE EMISSIVE PROPERTIES OF *trans*-3-STYRYLQUINOLINE IN NEUTRAL AND ACIDIC SOLUTIONS [†]

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Summary

The wavelength dependence of the fluorescence quantum yields of *trans*-3-styrylquinoline and of its protonated form has been studied in solvents of different polarity and hydrogen-bonding characteristics. The results obtained show that in all the examined solvents *trans*-3-styrylquinoline, in both neutral and protonated forms, exists as a mixture of two conformational isomers. The fluorescence lifetimes, emission and trans → cis photoisomerization quantum yields strongly depend on the solvent but they show no unequivocal correlation with its properties.

1. Introduction

In solutions of *trans*-1,2-diarylethylenes, conformational isomers (conformers and rotamers) originating from rotation of the aromatic rings around the quasi-single bond between the aryl group and the ethylenic carbon are present as an equilibrium mixture [1, 2]. For the aza analogues of diarylethylenes (pyridyl and quinolyl derivatives) the existence of conformers was first reported by Fischer and Fischer [3].

In a previous paper [4], we gave evidence for the existence of conformational isomers

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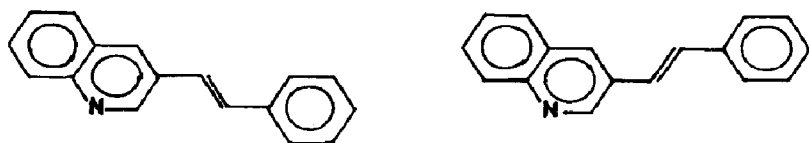
of *trans*-3-styrylquinoline (3-StQ) from a study of the dependence of its fluorescence (ϕ_f) and trans → cis photoisomerization (ϕ_c) quantum yields on the excitation wavelength.

We also found that the values of ϕ_f and ϕ_c strongly depend on the nature of the solvent. These variations may be attributed either to an influence of the solvent on the deactivation paths of the two rotamers or to a shift in the conformational equilibrium, possibly due to a different degree of solvation of the rotational isomers. Moreover, in aqueous media (pH 8), where some of 3-StQ molecules attain the prototropic equilibrium pertaining to their singlet excited state and emit as the cationic form, the quantum yield of the emission of the acidic form is, especially for long excitation wavelengths, practically the same as that obtained at pH 1 when 3-StQ is fully protonated in the ground state. This was attributed to a shift of the conformeric equilibrium in acidic media towards the poorly fluorescent rotamer.

Lastly, in aqueous media, at a fixed λ_{exc}, some variation in the ϕ_f with the water-to-ethanol ratio in the buffer solution was observed.

These facts prompted us to determine the fluorescence quantum yields of 3-StQ and of its protonated form (3-StQH$^+$) in a series of solvents of different polarity and hydrogen-bonding ability. The aim was to determine if the solvent affects the equilibrium or the excited state deactivation parameters of the rotational isomers.

2. Experimental details

3-StQ is the same as was utilized in previous studies [4, 5]. Cyclohexane, ethanol (EtOH), methanol (MeOH), 1- and 2-propanol and 1,1,1-trifluoroethanol (TFE) were Carlo Erba RS products and were used as received. Acetonitrile (RP grade) was distilled over P_2O_5 and then distilled again from anhydrous K_2CO_3.

Fluorescence and photoisomerization quantum yields and fluorescence lifetimes were measured at room temperature (20 ± 2 °C) in air-saturated solutions. The ϕ_f were determined with a Perkin–Elmer MPF 44 spectrophotofluorometer equipped with an accessory for spectra correction, using cyclohexane solutions of 9,10-diphenylanthracene ($\phi_f = 1$ [6]), 2-(1-naphthyl)-5-phenyl-1,3,4-oxadiazole ($\phi_f = 0.7$ [6]) and a 0.1 N H_2SO_4 solution of quinine sulphate ($\phi_f = 0.55$ [7]) as standards. The ϕ_f obtained with the three standards agree to within 10%. No correction for the differences in refractive index was made [8]. The optical density of the solution was always less than 0.05 in a cell 1 cm thick. The values reported are each the

average of three independent runs; the mean deviation did not exceed 5%. Fluorescence spectra and quantum yields for 3-StQH$^+$ were obtained in solvents containing 0.1 M H_2SO_4, except for cyclohexane and acetonitrile which contained 0.1 M CCl_3COOH.

Fluorescence lifetimes were measured using a single-photon counting apparatus obtained from Applied Photophysics.

The photoisomerization quantum yields were determined under conditions in which the incident light was totally absorbed. The light source was a stabilized high pressure xenon arc (Osram XBO 150W) from which the exciting wavelength was isolated using narrow band interference filters (Ealing). The intensity of the incident radiation was determined by ferrioxalate actinometry [9]. Irradiations were carried out up to about 10% conversion. The conversion percentages were determined by UV spectrophotometry after suitable dilution of the irradiated solutions. The ϕ_c values reported are each the average of five independent runs; the mean deviation was 7%.

3. Results and discussion

3.1. Neutral trans-3-styrylquinoline

The absorption spectrum of 3-StQ in cyclohexane, EtOH and 95vol.%-H_2O-5vol.%EtOH is reported in Fig. 1. Looking at the main transitions, one can see that the benzenic band, peaking at 280 nm in cyclohexane, shifts to 283 - 284 nm in hydroxylic solvents; the ethylenic band at 315 nm is practically unaffected by the solvent and the transition centred at 360 nm (quinolinic in nature) is red shifted in polar solvents. Moreover, the molar extinction coefficients generally increase on going from cyclohexane to water, the extent of the variation being different for the three bands. Molar extinction coefficients at three selected wavelengths in various solvents are
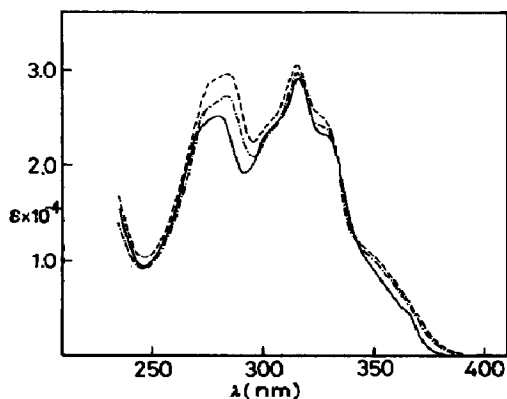

Fig. 1. Absorption spectra of 3-StQ in cyclohexane (———), EtOH (— · —) and 95vol.%-H_2O—5vol.%EtOH (— — —).

TABLE 1

Molar extinction coefficients for selected wavelengths of the benzenic (280 nm), ethylenic (315 nm) and quinolinic (360 nm) bands of 3-StQ in solvents of different dielectric constant ϵ

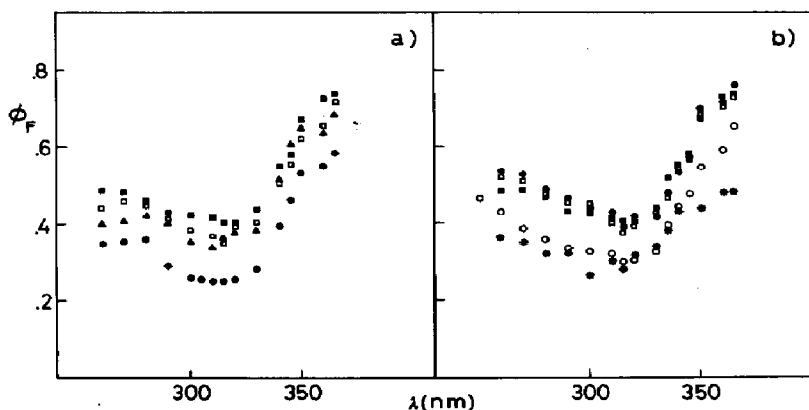| Solvent	280 nm	315 nm	360 nm	ϵ
Cyclohexane	25200	29050	5650	2.023
Ethyl acetate	25700	30700	6150	6.02
EtOH	26700	29700	7050	24.058
Acetonitrile	27200	32000	6100	37.5
MeOH	28200	30100	7200	32.7
H$_2$O	29200	30600	7300	80.2

Fig. 2. (a) Fluorescence quantum yields of 3-StQ in different solvents: ●, cyclohexane; ▲, acetonitrile; ■, EtOH; □, MeOH. (b) Fluorescence quantum yields of 3-StQ in different 1 M KOH–EtOH mixtures: *, 98vol.%–2vol.%; ○, 80vol.%–20vol.%; ●, 50vol.%–50vol.%; □, 20vol.%–80vol.%; ■, absolute EtOH.

collected in Table 1: they substantially increase for the benzenic and the quinolinic bands, while they remain practically constant for the ethylenic transition. A possible explanation of the variations in the absorption spectrum of 3-StQ with the solvent could be the composition of the rotamer equilibrium mixture being different in the various solvents. In fact, the two rotamers of 3-StQ have very different absorption spectra, as shown by the fluorescence excitation spectra obtained in cyclohexane solution [4]. One of the rotamers (A) has strong absorption at 270 - 280 nm and at λ > 340 nm and emits at long wavelengths with a high quantum yield (about 0.6); the other rotamer (B) has strong absorption at 315 nm, a low fluorescence quantum yield and emission hypsochromically shifted with respect to that of the conformer A. If one supposes that in polar and hydrogen-bonding solvents the rotamer composition is enriched in the most fluorescent conformer A, the observed spectral variations in the 3-StQ absorption spectrum can be understood. The increase in the fluorescence quantum yield on going from apolar to polar or hydrogen-bonding solvents (see Fig. 2(a)) seems to
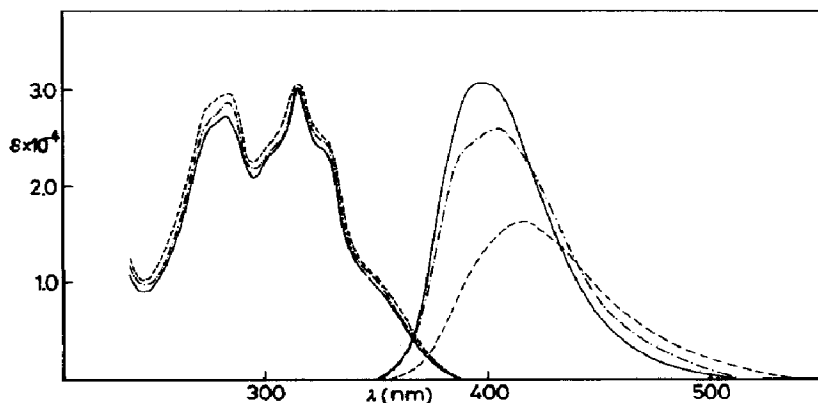
Fig. 3. Absorption and fluorescence emission spectra of 3-StQ in EtOH (———), and in H₂O–EtOH mixtures (— · —, 50vol.%–50vol.%; — — —, 98vol.%–2vol.%). The emission spectra were recorded at λ_{exc} = 345 nm.

confirm the above hypothesis. However, in all the examined solvents, the ratio between the maximum and the minimum fluorescence quantum yields (at λ_{exc} = 360 nm and λ_{exc} = 315 nm respectively) is practically the same (about 2). This seems to indicate that the variation in ϕ_f is not due to an appreciable change in the conformer composition (otherwise solutions enriched in the rotamer A should show a levelling of the fluorescence quantum yields with increasing λ_{exc}).

The variation in ϕ_f in 1 M KOH–EtOH mixtures (reported in Fig. 2(b)) shows no correlation either with the dielectric constant or with the hydrogen-bonding characteristics of the medium. In fact, for all excitation wavelengths, the ϕ_f remain practically unchanged on going from pure ethanol (ϵ = 24.6) to 50vol.%KOH–50vol.%EtOH (ϵ = 64.2) and drop considerably at lower EtOH concentrations. In cyclohexane and 1 M KOH the ϕ_f are about the same. The hypothesis of a very similar conformer composition in cyclohexane and in KOH does not satisfactorily account for the similarity between the ϕ_f. In contrast with the above hypothesis, there is a steady modification over the whole wavelength range of the absorption spectrum in H₂O–EtOH mixtures, and there is a progressive red shift of the emission with increasing H₂O concentration (Fig. 3). The emission of 3-StQ is π,π^* in nature, so a red shift of the fluorescence with increasing solvent polarity is expected; however, the extent of the fluorescence shift (about 20 nm) compared with that of the absorption spectrum (about 2 nm) suggests that there is a contribution to the observed emission shift, besides the normal polarity effect, from an enrichment of the mixture in the long-wavelength-emitting A conformer. The increase in the A content in the mixture should be accompanied by an increase in the overall fluorescence yield, but this is not observed. However, it is not be expected that the solvent affects only the conformer composition of 3-StQ. For stilbene-like molecules [2] it has been found that the solvent effect on the excited state deactivation kinetic parameters is large. In particular, for the hydrocarbon homologue of 3-StQ, 2-

styrylnaphthalene, k_f and ϕ_f of one of the rotamers in EtOH are markedly depressed with respect to the values in n-hexane [10] (an opposite effect was observed for the other rotamer); only minor variations in the relative abundance of the two isomers in the different solvents were observed. Hence, in 3-StQ, a dependence of the kinetic parameters of the excited states on the nature of the solvent should be expected given also the presence of the heterocyclic nitrogen, a site of hydrogen bonding in the solvent cage. However, in our opinion, the spectral shifts and the fluorescence quantum yield changes in the examined solvents are, in part, due to a variation in the rotamer composition. This variation cannot be directly determined because the fluorescence lifetime of one of the conformers is too short to be measured with our apparatus. (The fluorescence lifetimes of the two conformers of 3-StQ in cyclohexane solution are 0.4 and 2.3 ns.) This prevents us obtaining the relative abundance of the rotamers by applying the approach adopted by Birks *et al.* [11] based on the analysis of the bi-exponential decay parameters of the conformers of 2-styrylnaphthalene.

3.2. trans-3-Styrylquinolinium cation

The absorption spectra of 3-StQ in aqueous acidic media with different EtOH concentrations and in cyclohexane containing CCl_3COOH (0.1 M) are shown in Fig. 4. There is a general red shift of the spectrum with increasing EtOH content and a further red shift in cyclohexane. In particular, the batochromic band has its absorption maximum at 390 nm in cyclohexane, at 380 nm in H_2O–EtOH mixtures whose EtOH concentration is greater than 50 vol.% and at 370 nm in H_2). A similar bathochromic shift of the absorption spectrum of a charged species (3-StQH$^+$) with decreasing
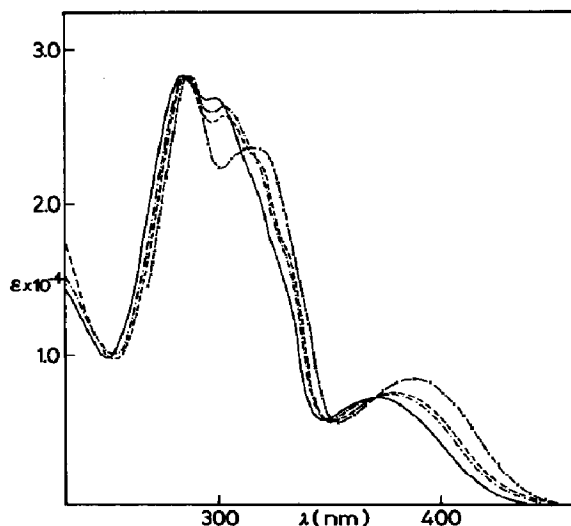

Fig. 4. Absorption spectra of 3-StQH$^+$ in H_2O–EtOH mixtures (———, 99vol.%–1vol.%; — · —, 50vol.%–50vol.%; — — —, 1vol.%–99vol.%) and in cyclohexane plus 0.1 M CCl_3-COOH (—×—).
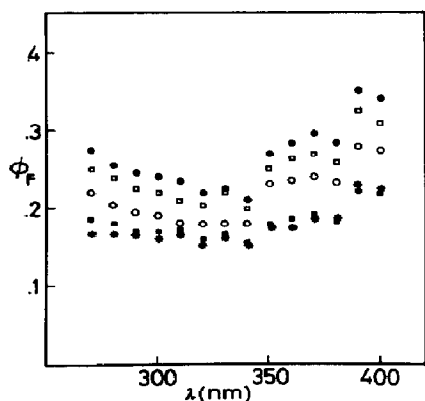
Fig. 5. Fluorescence quantum yields at various λ_{exc} of 3-StQH$^+$ in 0.1 M H$_2$SO$_4$–EtOH mixtures: *, 99vol.%–1vol.%; ○, 80vol.%–20vol.%; ●, 50vol.%–50vol.%; □, 20vol.%–80vol.%; ■, 1vol.%–99vol.%.

TABLE 2

Trans → cis photoisomerization quantum yields of 3-StQH$^+$ in different H$_2$O–EtOH mixtures at four selected excitation wavelengths

Ethanol (vol.%)	ϕ_c^{280}	ϕ_c^{315}	ϕ_c^{340}	ϕ_c^{380}
5	0.06$_5$	0.08$_5$	0.11$_5$	0.07$_5$
15	0.07	0.09	0.11$_5$	0.08
50	0.08$_5$	0.11	0.13$_5$	0.09
80	0.08$_5$	0.11	0.13$_5$	0.10
95	0.05$_5$	0.09$_5$	0.12	0.08$_5$

solvent polarity can only be understood if it is indicative of a variation in the conformer composition.

The variations in the absorption spectrum in H$_2$O–EtOH are also accompanied by changes in ϕ_f at the various λ_{exc}. In the whole excitation range explored, the ϕ_f increase with increasing EtOH concentration up to 50 vol.%; for higher EtOH concentrations, the ϕ_f decrease and the ϕ_f are the same in 99 vol.% EtOH as in 99 vol.% H$_2$O (see Fig. 5). For the protonated molecule, as for the free base, there is a contrast between the changes in the absorption spectrum and the ϕ_f with the composition of the H$_2$O–EtOH mixture. While the trend in the absorption spectra points to an enrichment of the mixture in the long-wavelength-absorbing rotamer, the variations in the ϕ_f show no monotonic dependence on the EtOH content in the solution, so that an influence of the medium on the deactivation parameters can be safely hypothesized. In agreement with the above hypothesis, the values of trans → cis photoisomerization quantum yields, collected in Table 2 for a number of excitation wavelengths, show a dependence on EtOH content similar to that of ϕ_f. On going from H$_2$O to EtOH, the ϕ_c at first increase (up to 50 vol.% EtOH) and afterwards decrease in the same way as the ϕ_f. Therefore, a com-
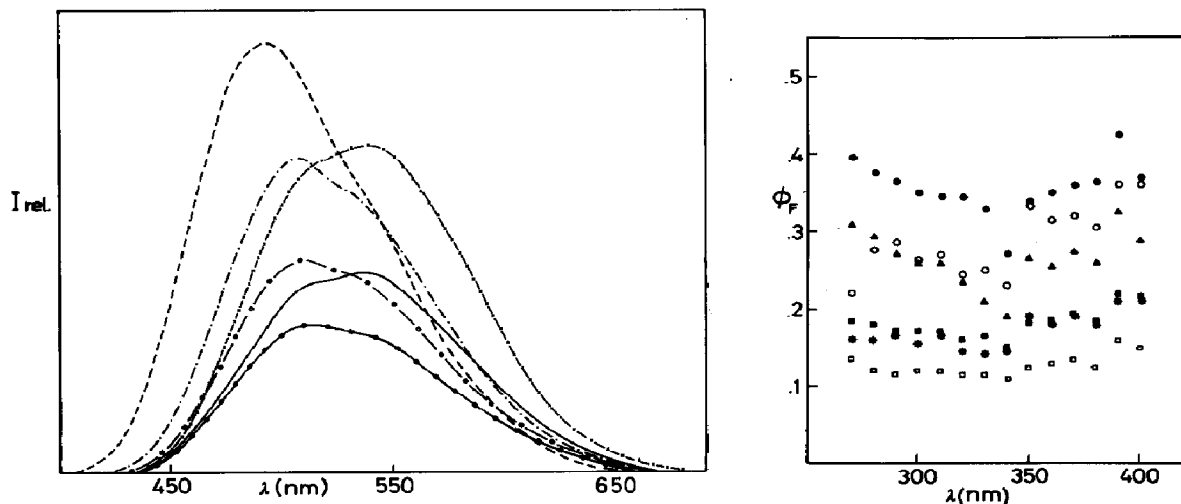
Fig. 6. Fluorescence emission spectra of 3-StQH$^+$ in cyclohexane (— — —), acetonitrile (—×—), 2-propanol (— · —), EtOH (—○—), MeOH (—●—) and 98vol.%H$_2$O–2vol.%EtOH (———). λ_{exc} = 390 nm.

Fig. 7. Fluorescence quantum yields at different λ_{exc} of 3-StQH$^+$ in MeOH (□), 99vol.%-H$_2$O–1vol.%MeOH (*), 2-propanol (▲), cyclohexane (●), acetonitrile (○) and EtOH (■).

parative examination of the dependence of ϕ_f and ϕ_c on the solvent composition shows that the variation in the photochemical and photophysical properties of 3-StQH$^+$ in solution cannot be interpreted by the oversimplified model of a change in the conformational equilibrium between the two species A and B that have opposite fluorescence and photoisomerization characteristics.

The influence of the solvent on the emissive properties of 3-StQH$^+$ is summarized in Figs. 6 and 7. As one can see from these figures, there is a strong dependence of the spectral shape, wavelength of maximum emission and fluorescence yield on the solvent. Although the very broad maximum in all the solvents, except cyclohexane, could suggest the presence of two emitting species, only one emission lifetime was found in each case. The values of the fluorescence lifetimes in various solvents are collected in Table 3. In H$_2$O, a 35-fold reduction in the emission intensity (obtained by adding 1 M KBr to the 3-StQH$^+$ solution) does not appreciably modify the spectral distribution of the emission. However, the excitation spectrum of the short wavelength emission (440 - 450 nm) is, in the spectral range 290 - 350 nm, red shifted (by about 4 - 5 nm) and, above 350 nm, is slightly blue shifted (by about 2 nm) with respect to the excitation spectrum of the fluorescence of $\lambda_{em} > 450$ nm. In all the H$_2$O–EtOH mixtures the long wavelength part of the excitation spectrum (350 - 400 nm) undergoes a red shift which is the same as that observed in the absorption spectrum. All the above facts indicate that in practice only one conformer appreciably emits at room temperature. The presence of two conformers is confirmed by the variations in ϕ_f and ϕ_c with λ_{exc} and by the fluorescence excitation spectra at 77 K in

TABLE 3

Fluorescence lifetimes for 3-StQH$^+$ in different air-equilibrated solvents (λ_{exc} = 340 nm; λ_{em} = 490 nm)

Solvent	τ (ns)
Cyclohexane	8.2
2-Propanol	7.0
Acetonitrile	8.9
EtOH	4.5
MeOH	3.4
H$_2$O (plus 1 vol.% MeOH)	5.1
Trifluoroethanol	9.9

rigid glasses composed of 3-methylpentane (0.1 M CCl$_3$COOH) or 50vol.%-MeOH–50vol.%EtOH (1% HClO$_4$). In both glasses the emission is strongly blue shifted (to 445 nm in EtOH–MeOH and 460 nm in 3-methylpentane) with respect to the emission in fluid solution at room temperature (owing to the lack of solvent reorganization around the excited molecule) and the excitation spectrum of the short wavelength emission has a vibrational structure which is buried in a structureless absorption in the excitation spectrum of the longer wavelength emission.

The strong dependence of ϕ_f on the medium is not easily related to any given property of the solvent, and in particular not to the dielectric constant ϵ. The ϕ_f in acetonitrile (ϵ = 37.5) are about three times higher than in MeOH (ϵ = 32.04) and about 1.5 times higher than in H$_2$O (ϵ = 80); moreover, in 2-propanol (ϵ = 19.9) the fluorescence yield is about 1.5 times higher than in the homologous 1-propanol (ϵ = 20.33).

The dependence of ϕ_f of both the basic and the protonated form of 3-StQ in an aqueous medium on the ethanol content is especially intriguing. The values in 50vol.%H$_2$O–50vol.%EtOH are about 50% higher than the corresponding values in 99vol.%H$_2$O–1vol.%EtOH for both the neutral and the charged molecule; this rules out the possibility that the formation of some sort of complex is responsible for the variations. (However, the ratios ϕ_f(H$_2$O–EtOH)/ϕ_f(H$_2$O) for [EtOH] $\neq$ 50 vol.% are not the same for the basic and acidic forms.) This dependence forced us to reconsider the results and the conclusions of our previous paper [4] on the influence of an acidic medium on the rotamer composition in solution. The conclusions drawn in ref. 4 were based on a comparison of the ϕ_f obtained for 3-StQ in 0.1 M HClO$_4$ and 1 M KOH, both containing 15 vol.% EtOH, with the values for the basic and the acidic part of the emission in Britton buffer (pH 8) containing 10 vol.% EtOH. At this pH, 3-StQ is partially protonated in the singlet excited state: the extent of the equilibration depends on the EtOH content, as found for 3-styrylpyridine [12] and naphthylpyridylethylenes [13]. Given the dependence of ϕ_f on the alcohol content, which is different for the basic and the acidic forms, we measured ϕ_f in 1% H$_2$SO$_4$, 1 M KOH and in Britton buffer at pH 8, all containing 2 vol.% MeOH (the alcohol

TABLE 4

Wavelength dependence of the fluorescence quantum yields of 3-StQ in Britton buffer at pH 8 containing 2 vol.% methanol

λ (nm)	ϕ_{tot}	ϕ_b	$1 - \phi_b/\phi_b{}^0$	$(\phi_a{}^0)_{calc}$
270	0.25	0.11$_5$	0.66$_5$	0.20
280	0.24$_5$	0.11	0.65	0.20
290	0.24	0.10$_5$	0.67	0.20
300	0.22	0.09	0.66	0.20
310	0.22	0.09	0.69	0.18$_5$
320	0.21	0.09	0.71	0.17
330	0.23$_5$	0.10$_5$	0.69$_5$	0.19
340	0.32$_5$	0.15	0.67	0.26
350	0.31$_5$	0.15	0.68	0.23$_5$
370	0.36$_5$	0.19	0.55$_5$	0.31

ϕ_{tot}, total emission quantum yield; ϕ_b, emission as free base; $1 - \phi_b/\phi_b{}^0$, fraction of the excited molecules which emit as the cationic form (see ref. 4); $(\phi_a{}^0)_{calc}$, emission quantum yield calculated with the hypothesis of a total protonation of the excited molecules.

most similar to H_2O). The results obtained are collected in Table 4 (in which the values of ϕ_f are also reported, these being calculated according to the procedure described in ref. 4 for the acidic form using the hypothesis that all the molecules attain prototropic equilibrium in the excited state). A comparison with the values reported in our previous paper shows, as expected, that a decrease in alcohol content allows more molecules to attain equilibrium with the protons in the excited state. The difference between the found and calculated values for ϕ_f of the acidic form is not, however, so dramatic as that found previously; the shift in conformeric equilibrium seems to be confirmed, but its value is much lower.

3.3. Trifluoroethanol as the solvent

TFE is a strong hydrogen-bonding donor solvent [14] but its pK_a of 12.4 [15] is high enough to leave 3-StQ in the ground state as a free base. This is confirmed by the absorption spectrum reported in Fig. 8 together with that of the molecule in TFE plus 1% H_2SO_4: the basic features of the spectra are very similar to the spectrum of the free and protonated 3-StQ in H_2O–EtOH mixtures. However, the fluorescence emission spectra and the lifetimes are in both TFE and TFE plus 1% H_2SO_4 typical of the protonated styrylquinoline. The emission band is structureless with a maximum at 510 nm (at short emission wavelengths a residual free-base emission (below 1%) is observed in pure TFE). This means that in TFE the electronically excited 3-StQ is almost completely protonated. The variations in the fluorescence excitation spectra with the emission wavelength are similar, in both TFE and TFE plus 1% H_2SO_4, to those described for alcoholic solvents. The fluorescence quantum yields in TFE and TFE plus 1% H_2SO_4 are collected
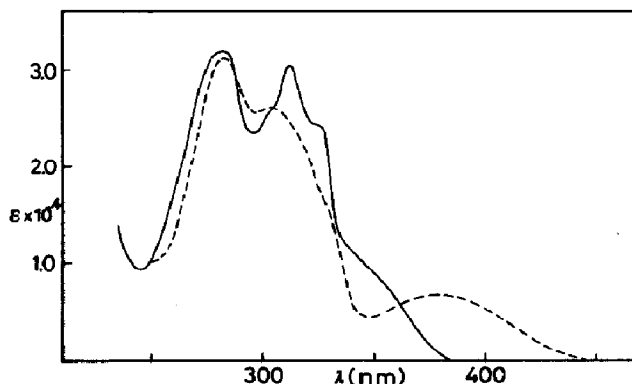
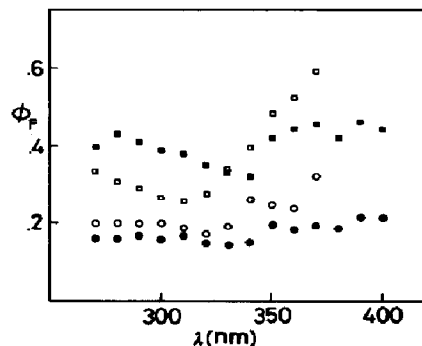Fig. 8. Absorption spectra of 3-StQ in TFE (———) and of 3-StQH⁺ in TFE plus 1% H_2SO_4 (— — —).

Fig. 9. Fluorescence quantum yields of 3-StQH⁺ in TFE (□), TFE plus 1% H_2SO_4 (■), H_2O plus 1% H_2SO_4 (●) and Britton buffer at pH 8 (○).

in Fig. 9: for both the neutral and the charged form of 3-StQ an excitation-wavelength dependence of ϕ_f is observed. In TFE, in particular, the minimum of the fluorescence efficiency occurs at 310 nm, as in all other examined solvents in which 3-StQ emits as a free base. This means that also the charged form of the conformer, with a low ϕ_f in non-protonating solvents, has a low emission quantum yield. The ϕ_f in TFE are higher than in TFE plus 1% H_2SO_4 for $\lambda_{exc} > 330$ nm and are lower for $\lambda_{exc} < 330$ nm. This behaviour is different from that in aqueous solvents (also reported in Fig. 9 for comparison), in which the yields for the acidic form calculated from the emission spectra at pH 8 (vide supra) are always higher than those found for 3-StQH⁺ in 1% H_2SO_4. A comparison of such behaviour of the ϕ_f in TFE and in aqueous media does not lead to the conclusion that the conformeric equilibrium is more shifted towards the poorly fluorescent conformer for protonated forms than for the free base. If so, on going from the free base to the acidic form, parallel behaviour of the quantum yields in water and in TFE should be observed.

4. Conclusions

The results of this steady state study of the emission properties of solutions of both 3-StQ and 3-StQH⁺ in different solvents show that the fluorescence yield is strongly dependent on the nature of the solvent. This dependence is not easily correlated with the properties of the medium, in particular its polarity and hydrogen-bonding ability. In this respect, especially intriguing are the properties of both the free base and the protonated form of 3-StQH in H_2O–EtOH mixtures.

The fluorescence excitation spectra and the dependence of the emission quantum yields on the excitation wavelength show that, in all the examined media, two conformers are present in solution. However, the results obtained

do not allow any definitive conclusion to be drawn about the influence of the solvent and protonation on the conformer equilibrium in solution.

Acknowledgments

References

1 E. Fischer, *J. Photochem., 17* (1981) 231.
2 U. Mazzucato, *Pure Appl. Chem., 54* (1982) 1705.
3 G. Fischer and E. Fischer, *Bull. Soc. Chem. Belg., 88* (1979) 889.
4 G. Galiazzo, G. Gennari and P. Bortolus, *J. Photochem., 23* (1983) 149.
5 G. Gennari, G. Galiazzo and G. Cauzzo, *J. Photochem., 5* (1976) 409.
6 J. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules,* Academic Press, New York, 1965, pp. 130, 158.
7 R. A. Velapoldi and K. D. Mielenz, *Natl. Bur. Stand. Spec. Publ., 260-64* (1980).
8 F. J. Busselle, N. D. Haig and C. Lewis, *Chem. Phys. Lett., 72* (1980) 533.
9 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A, 235* (1956) 18.
10 G. Bartocci, F. Masetti, U. Mazzucato and G. Marconi, *J. Chem. Soc., Faraday Trans. II, 80* (1984) 1093.
11 J. B. Birks, G. Bartocci, G. G. Aloisi, S. Dellonte and F. Barigelletti, *J. Chem. Phys., 51* (1980) 113.
12 U. Mazzucato, F. Masetti and G. Favaro, *Gazz. Chim. Ital., 105* (1975) 1177.
13 G. Favaro, F. Masetti, U. Mazzucato and P. Bortolus, *J. Phys. Chem., 79* (1975) 2785.
14 M. J. Kamlet, J. L. Abboud and R. W. Taft, *J. Am. Chem. Soc., 99* (1977) 6027.
15 M. F. Anton and W. R. Moomaw, *J. Chem. Phys., 66* (1977) 1808, and references cited therein.