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Protonation dependent electron transfer in 2-styrylquinolines

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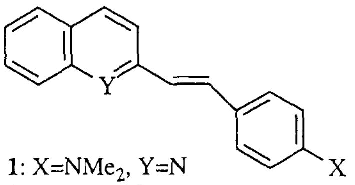
Abstract

The absorption and emission spectra for 4′-substituted-2-trans-styrylquinoline (X = NMe_2, **1**; H, **2**; CN, **3**; NO_2, **4**) and 4′-N,N-dimethylamino-2-trans-styrylnaphthalene **5** were studied in various solvents and at various acid concentrations. Monoprotonated or doubly protonated forms of **1** are present depending on the acid concentration. Excited state deprotonation of the doubly protonated form of **1** is observed in aprotic dichloromethane solvent. This excited state deprotonation process can be prevented by introducing protic methanol to the aprotic solvent media.

1. Introduction

The photophysical aspects of intramolecular charge transfer interaction continue to attract attention [1–3]. For example, the twisted intramolecular charge transfer (TICT) for the push–pull stilbene system has been studied [4,5]. The dipole moment of the excited state is greater than that of the ground state and is sensitive to the environment [6–8]. The styrylquinoline derivatives [9] and styrylnaphthalene show a behavior similar to the stilbene system. Dual fluorescence has recently been reported [10] for this system.



1: X=NMe_2, Y=N
2: X=H, Y=N
3: X=CN, Y=N
4: X=NO_2, Y=N
5: X=NMe_2, Y=CH

In this Letter the absorption and emission spectra of neutral and acidic 4′-substituted-2-trans-styrylquinoline (**1–4**) and 4′-N,N-dimethylamino-2-trans-styrylnaphthalene **5** are studied.

2. Experimental

2.1. Materials

Compounds **1** to **5** were prepared by known procedures. Quinaldine and *p*-substituted benzaldehyde in acetic anhydride were refluxed for 20 h [11]. The solid product was purified by column chromatography and recrystallized from benzene. Compound **5** was prepared by Wittig condensation of *p*-N,N-dimethylaminobenzaldehyde with 2-methylenenaphthalene triethyl phosphonium ylides. The yellow solid product was recrystallized from benzene. All the solvents were of Uvasol grade, and hydrochloric acid was suprapure grade from Merck and was used as received.

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2.2. Method

UV–visible absorption spectra were recorded on a Hitachi U-2000 spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-3000 fluorescence spectrometer. A typical concentration of 1.5×10^{-5} M was used for the measurements. The hydrochloric acid was dissolved in ethyl acetate (EA) solution and was added to the organic phase at a volume of less than 3%.

3. Results

The fluorescence spectra of compound **5** in a series of solvents are shown in Fig. 1. The absorption and fluorescence maxima in various solvents at room temperature are collated in Table 1. The absorption maxima are not sensitive to solvent polarity. The fluorescence spectra are structureless and have a bathochromophoric shift in polar solvents. This is a typical emission for an intramolecular charge transfer (ICT) state. The fluorescence spectra of compound **1** in various solvents are similar to that of compound **5**.

The ground and excited state dipole moments for the ICT systems can be calculated [12] from the Stokes shifts in the absorption and emission frequencies and the solvent polarity function $f(\varepsilon, n)$ (Eq. 1), where ε and n represent the dielectric and refractive constants. The ground and excited state dipole moments thus calculated for compound **1** are 4 and 19 D respectively (3 and 16 D for compound **5**).

$$f(\varepsilon, n) = \frac{2n^2+1}{n^2+1}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right). \qquad (1)$$

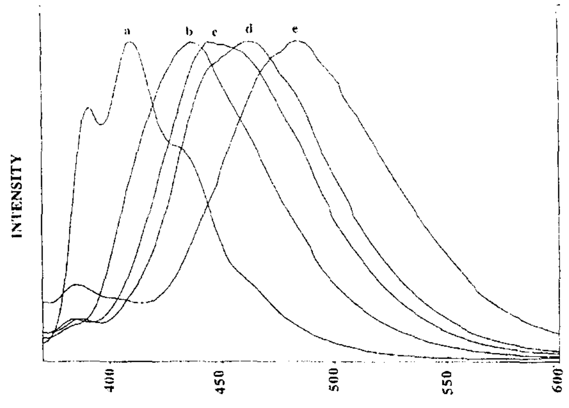


Fig. 1. Emission spectra of compound **5** in different solvents (exc: 320 nm): (a) n-hexane; (b) ether; (c) EA; (d) dichloromethane; (e) acetonitrile.

In acidic EA ($[H^+] = 3.8 \times 10^{-5}$ M), compounds **1** and **5** show quite different behaviors (Figs. 2 and 3). Protonation in the N,N-dimethylamino group will change the donor ability and destroy the electron transfer behavior [13] in compound **5**. The ICT emission band disappears and shows a strong emission band with fine structure. It is assigned as a locally excited (LE) state emission. There are two basic sites in compound **1** – the quinoline and N,N-dimethylaniline groups. Usually, the N,N-dimethylaniline site is more basic than the quinoline site. However, with the involvement of charge transfer in the ground state of compound **1**, the quinoline site becomes more basic than the N,N-dimethylaniline site. Thus the quinoline nitrogen atom is protonated before the N,N-dimethylaniline site.

Table 1
Absorption and fluorescence maxima of compound 1 and compound 5 in different solvents

		CH_3CN	CH_2Cl_2	THF	EA	ether	n-butyl ether	hexane
compound 5	absorption (nm)	363 287	367 288	365 287	359 285	358 288	360 286	358 285
	fluorescence (nm)	485	463	458	446	438	430	391 410
compound 1	absorption (nm)	387 289 253	392 290	387 289 252	384 288	382 285 252	386	375 288 249
	fluorescence (nm)	538	508	501	495	480	460	406 429

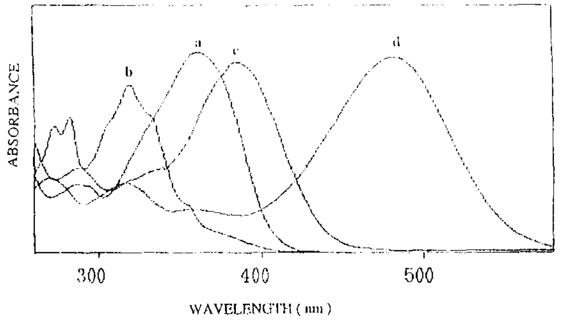


Fig. 2. Absorption spectra of: (a) compound **5** in neutral EA solvent; (b) compound **5** in acidic EA solvent (HCl = 2×10^{-4} M); (c) compound **1** in neutral EA solvent; (d) compound **1** in acidic EA solvent (HCl = 5×10^{-4} M).

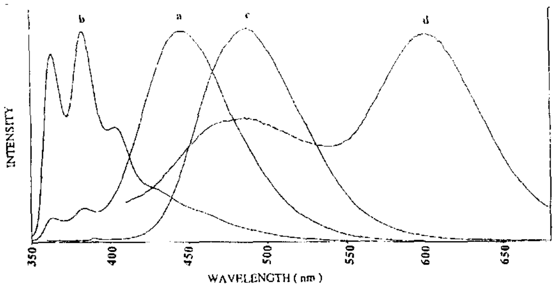


Fig. 3. Emission spectra of: (a) compound **5** in neutral EA solvent; (b) compound **5** in acidic EA solvent (HCl = 2×10^{-4} M); (c) compound **1** in neutral EA solvent; (d) compound **1** in acidic EA solvent (HCl = 5×10^{-4} M). Spectra are uncorrected (exc: 340 nm).

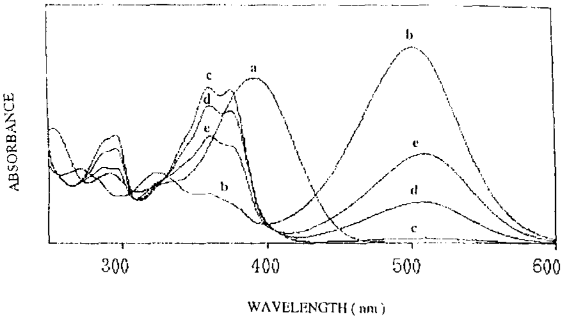


Fig. 4. Absorption spectra of compound **1** in CH_2Cl_2 under different conditions: (a) neutral solvent; (b) 3.8×10^{-5} M HCl; (c) 2×10^{-3} M HCl; (d) 2×10^{-3} M HCl+0.4 M CH_3OH; (e) 2×10^{-3} M HCl+0.7 M CH_3OH.

When the quinoline group is protonated, the electron pulling ability will be stronger and will show a large red-shift in the charge transfer (CT) absorption and emission spectra. Protonation at different sites in compounds **1** and **5** shows opposite behaviors in the absorption and emission spectra, as shown in Fig. 2 and Fig. 3.

At a higher concentration of the acid ($[H^+] = 2\times10^{-3}$ M), protonation can continue to occur in the N,N-dimethylamino group of compound **1**, and the ICT effect disappears, the LE state becomes the lowest fluorescent excited state. Fig. 4 shows the influence of different acidities on the absorption spectra of compound **1** in dichloromethane. The CT absorption band of protonated compound **1** only

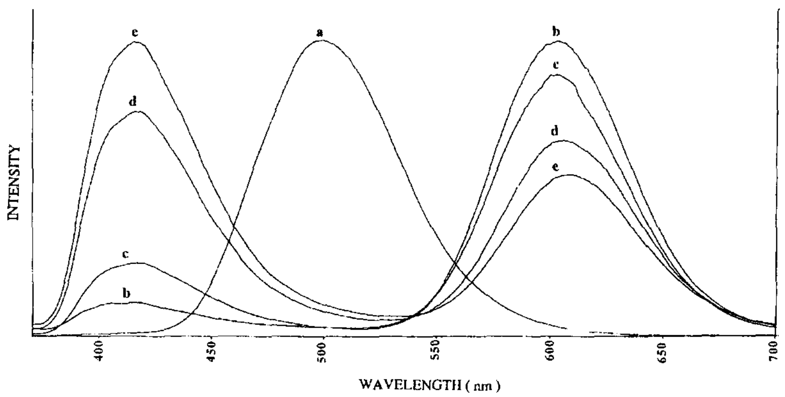


Fig. 5. Emission spectra of compound **1** in CH_2Cl_2 under different conditions (exc: 360 nm): (a) neutral solvent; (b) 3.8×10^{-5} M HCl; (c) 2×10^{-3} M HCl; (d) 2×10^{-3} M HCl + 0.4 M CH_3OH; (e) 2×10^{-3} M HCl + 0.7 M CH_3OH. Spectra are uncorrected.

exists at lower acidic concentrations. When more acid was added, the CT band disappeared gradually and new structured bands at 362 and 370 nm appeared. These bands are assigned as the double protonation of **1** by comparison with the absorption spectra of protonated **3** and **4**. In dichloromethane, the protonated forms of compounds **3** and **4** both absorb at 362 and 370 nm, whereas that of compound **2** absorbs at 382 nm.

There are two emission bands for compound **1** in an acidic solvent. The fluorescence spectra of compound **1** in dichloromethane are shown in Fig. 5. The existence of protic solvents with suitable basicity will enhance the probability of deprotonation on the N,N-dimethyl group in the ground state, as shown in Fig. 4.

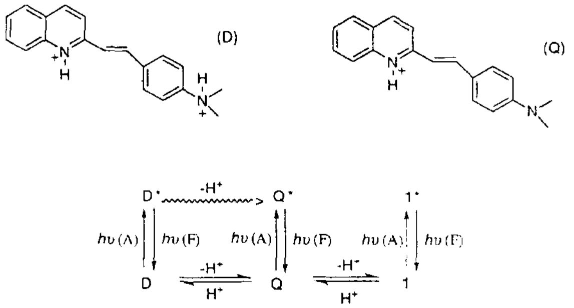
4. Discussion

The effects of protonation on the donor group have been observed for many bichromophoric and trichromophoric systems [17,18]. A protonation-induced masking effect of the lone pair electrons at the amino group in **5** has been reported [9].

Protonation of **5** destroyed the original ICT absorption band, and structured bands at 318, 282 and 272 nm appeared. This is similar to the absorption band in conjugated naphthalene.

There are two basic sites in **1**, which can be protonated in a medium of appropriate acidity. In a low acidity medium, the quinoline ring is first protonated then the N,N-dimethylamino group. When the acid concentration increases, the N,N-dimethylamino group can accept a second proton. In order to ensure that the double protonation really did occur in the ground state, **4**, **3** and **2** were synthesized so that their protonation absorption spectra could be measured. The maxima and shapes of the absorption spectra of **4** and **3** in their protonated forms can be matched with that of **1** at a high acid concentration, but those of **2** show a quite different behavior. The new band of **1** appearing at a high acid concentration is from the double protonation form [14].

Protonation in **1** will quench the original CT emission and two new emission bands appear. The higher energy fluorescence maximum (A band) is independent of solvent polarity and shows structured emission bands in a medium-polar solvent. The lower energy fluorescence maximum (B band) is structureless and shows a red-shift in a polar solvent. We assign the B band as a charge transfer emission band of single protonation in the quinoline ring of **1**, and the A band as a quinoline ring locally excited state emission resulting from the double protonation of **1** because of its similarity with neutral **1** in a nonpolar solvent. The excitation spectra of the A and B band emissions are similar between 270 to 400 nm. The B band also has a contribution from the CT absorption at 500 nm. The relationship between the neutral form of **1**, the monoprotonated form at the quinoline nitrogen (Q) and the doubly protonated form at both the aniline and quinoline nitrogen atoms (D) can be summarized as Scheme 1.



Scheme 1.

The equilibrium between D and Q in the ground state strongly depends on the environment. Greater acidity will favor the formation of D. The equilibrium between D and Q may be determined by the difference in basicity in different media.

For compound **1**, the protonation at the N,N-dimethylamino group will quench the charge transfer band, so that the emission from the double protonation of **1** will come from the quinoline ring locally excited state. The acidity of the corresponding N,N-dimethylaminium group in **1** will be larger in the excited than in the ground state, so the competition between deprotonation and emission will decide the deactivation of the excited state of D, with the relative intensity of the dual fluorescence depending on the environment, as shown in Fig. 5.

In dichloromethane solvent, the excited state deprotonation (D^* to Q^*) process is observable from the corresponding curve (Fig. 4b for absorption, Fig. 5b for emission). When methanol is present, the increase in the A band intensity is enhanced. This might be due to excited state deprotonation being prevented by the presence of methanol [15,16]. The pK_1 (quinoline) and pK_2 (N,N-dimethylamine) values measured for compound **1** are 5.95 and 2.82 respectively. The excited state pK_1^* and pK_2^* values obtained from the Forster cycle method are 18.3 and -12.7 respectively. This is consistent with the observation that the excited deprotonation process (D^* to Q^*) is observable from the more acidic N,N-dimethylaminium site. In a protic solvent or an aprotic solvent mixed with a protic solvent, the excited state deprotonation process of D^* does not readily occur.

5. Conclusion

The CT behavior of **1** is strongly dependent on the acid concentration. The equilibrium between mono and double protonation in the ground state for **1** is sensitive to the acidity of the medium. Excited state deprotonation of **1** is observable in aprotic dichloromethane solvent (D^* to Q^*). The excited state deprotonation process can be quenched by introducing methanol.

Acknowledgements

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