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Journal of Photochemistry and Photobiology A: Chemistry 151 (2002) 21–26

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Excited state proton transfer and steric effect on the hydrogen bonding interaction of the styrylquinoline system

Shun-Li Wang, Tai-Chen Lee, Tong-Ing Ho*

Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC

Received 20 August 2001; received in revised form 15 March 2002; accepted 23 March 2002

Abstract

The influence of hydrogen bonding (HB) and protonation on an intramolecular charge transfer (ICT) compound, such as *p-N,N*-dimethylamino-2-styrylnaphthalene (2-StN-NMe_2), *p-N,N*-diethylamino-2-styrylnaphthalene (2-StN-NEt_2), *p-N,N*-dimethylamino-2-styrylquinoline (2-StQ-NMe_2) and *p-N,N*-diethylamino-2-styrylquinoline (2-StQ-NEt_2), in the ground and excited state is investigated. The steric effect of HB on ICT compounds is studied in different protic acids. The steric and ICT effect will weaken the HB ability of the *N,N*-diethylamino site and enhance the HB ability of the quinoline site in 2-StQ-NMe_2. The excited state proton transfer (ESPT) occurred in the HB complex of 2-StQ-NMe_2. The excited state deprotonation (ESDP) process was observed for the double protonation form of 2-StQ-NMe_2 in 2,2,2-trichloroethanol (TCE). The influence between the HB interaction and protonation could be separated for the first time by using another strong base.

Keywords: Intramolecular charge transfer; ESDP; 2-StQ-NMe_2

1. Introduction

Intramolecular charge transfer (ICT) has been important in chemistry and biochemistry [1,2]. Hydrogen bonding (HB) plays an important role in the structuring of biochemical molecules such as DNA and proteins [3]. The study of HB interactions has been an extensively investigated topic [4–9]. The δ_c scale proposed by Taft describes the ability of the solvent to donate a proton in a solvent to a solute hydrogen bond [10]. Catalán employs the molecular thermodynamics of the gas and solution phases to achieve calorimetric quantification of the hydrogen-bond acidity of the solvent [11,12]. However, the HB complex may undergo proton transfer to form a protonated ion pair. In a solvent of strong HB ability, it is difficult to isolate the pure HB effect from the influence of protonation in the spectroscopic shift or solvation effect of the solvent [13]. Furthermore, the steric effect may interfere with the HB if the bonding site is too crowded [14]. So, there is some difference between the Taft δ_c value and the Catalán solvent acidity. The δ_c value for 2,2,2-trifluoroethanol (TFE) is higher than that for TCE, but according to Catalán, the latter has higher hydrogen-bond acidity.

The processes of ICT in the ground and excited state have been researched for a long time [2,15]. The ground state ICT can be observed by the charge transfer (CT) absorption band [16]. The excited state ICT is known as exciplex and has been well studied by Rettig and Baumann [17], Verhoeven and co-workers [18], Mataga et al. [19], and De Schryver and co-workers [20], among others. We have previously reported a study of the protonation-dependent ICT phenomenon of *p-N,N*-dimethylamino-2-styrylquinoline (2-StQ-NMe_2) system [21]. We would like to report the influence of HB and protonation effect on *p-N,N*-dimethylamino-2-styrylnaphthalene (2-StN-NMe_2), *p-N,N*-diethylamino-2-styrylnaphthalene (2-StN-NEt_2), *p-N,N*-diethylamino-2-styrylquinoline (2-StQ-NEt_2) and 2-StQ-NMe_2 [22] and the influence of solvent steric effect on HB interaction. The difference between HB and protonation effect was characterized by their influence on the electronic spectra of ICT compounds.

2. Experimental

Materials. Compounds 2-StQ-NMe_2 and 2-StQ-NEt_2 were prepared by known procedure. Quinaldine and *p*-substituted benzaldehyde in acetic anhydride were refluxed for 20 h [23]. The solid product was purified by column chromatography and recrystallized from benzene.

* Corresponding author. Fax: +886-2-2363-6359.
E-mail address: hall@chem50.ch.ntu.edu.tw (T.-I. Ho).

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PII: S1010-6030(02)00146-6

Compounds 2-StN-NMe_2 and 2-StN-NEt_2 were prepared by Wittig condensation of *p-N,N*-dialkylamino-benzaldehyde with 2-methylenenaphthalene triethyl phosphonium ylides. The yellow solid product was recrystallized from benzene. All the solvents were of Uvasol grade from Merck or spectrophotometric grade from ACROS and were used as received. The melting points of 2-StN-NMe_2 is 195–196 °C, 2-StN-NEt_2 is 129–130 °C, 2-StQ-NEt_2 is 101–104 °C (lit. 101–103 °C) [24] and 2-StQ-NMe_2 is 186–187 °C (lit. 184–185 °C) [24]. All the 2-StN and 2-StQ compounds are in their *trans* form.

Method. UV–visible absorption spectra were recorded on a Hitachi U-2000 spectrophotometer, and fluorescence spectra were obtained with a Hitachi F-3000 fluorescence spectrometer. Typical concentration for the chromophore used for the measurements was 1.5×10^{-5} M.

3. Results and discussion

The absorption spectra of 2-StN-NMe_2 in different solvents are shown in Fig. 1. In acetonitrile (Fig. 1a), the CT absorption band occurred at 363 nm. In TFE and 2,2,2-trichloroethanol (TCE), the CT bands are blue shifted to 329 and 325 nm, respectively (Fig. 1b and d). By comparison with the absorption maximum of the protonated 2-StN-NMe_2 in acetonitrile (321 nm) [21], it is obvious that the blue shifts in both TFE and TCE solvents are due to protonation or/and HB interaction at the electron donor (–NMe_2) site. In the presence of a large amount of triethylamine, the absorption maximum is not affected (Fig. 1c) in TFE, but is shifted from 325 to 340 nm in TCE (Fig. 1e). By considering the double well potential model, the equilibrium between HB and protonation depends on environment condition [25]. The equilibrium of HB and protonation of 2-StN-NMe_2 were shown in Scheme 1. From Scheme 1, the existence of HB or protonation complex depends on the concentration of solute molecules or proton donors in the system. The presence of a large amount of base, such as triethylamine in the system (Fig. 1) will reduce the concentration of proton obviously but show little change in solvent medium. So the equilibrium of protonation reaction is more favorable to dissociation in such situation. The result of dissociation will increase the concentration of 2-StN-NMe_2 and favor the reaction of HB. Therefore, we can use another strong base to delete the influence of protonation and increasing the HB interaction. In TCE, the protonated 2-StN-NMe_2 deprotonates in the presence of triethylamine and the HB interaction with pure solvent still remain. If more triethylamine is added to this system, there are no further shifts in the absorption maximum. In TFE, the blue shift is not affected by the addition of base indicating that the blue shift is primarily due to the HB interaction. Neither the absorption nor the emission spectra of the neutral 2-StN-NMe_2 were affected by adding triethylamine.

In the 2-StQ-NMe_2 system, there are two basic sites which include quinoline and *N,N*-dimethylamino group. Protonation or HB at the quinoline site will produce a large red shift in the absorption maximum, but a second protonation which occurred at *N,N*-dimethylamino site will produce a blue shift in the absorption spectra with fine structure. To understand the pure HB interaction of 2-StQ-NMe_2, the absorption maxima of 2-StQ-NMe_2 in different protic solvents which were mixed with acetonitrile in the presence of a large quantity of triethylamine are listed in Table 1. The equilibrium of HB interaction of 2-StQ-NMe_2 is shown in Scheme 2.

From Table 1, the absorption maxima of 2-StQ-NMe_2 in acetonitrile are red-shifted when the TFE content is increased. After the TFE content exceed 40% (v/v_0), the absorption maxima become blue shift. This result is primarily due to the HB interaction on different sites. The HB interaction at an acceptor of an ICT molecule causes a red shift in absorption maximum, but the interaction at a donor site shows the opposite effect. The extent of shift depend on the HB ability and the content of solvent. High HB and

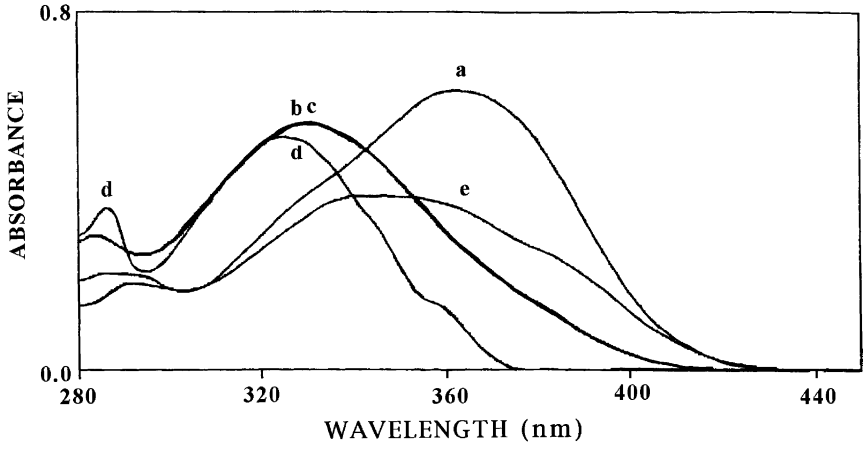
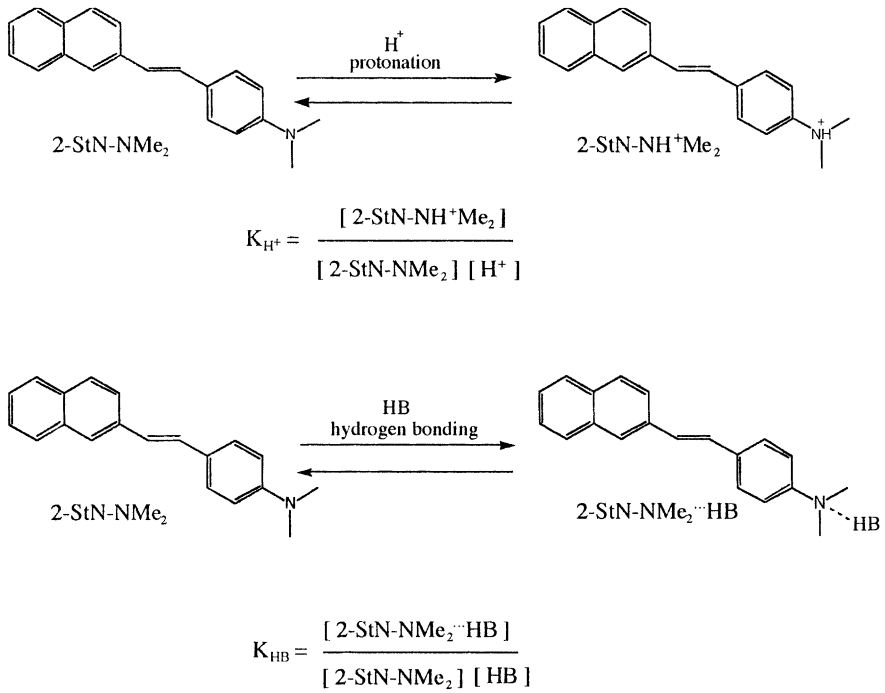


Fig. 1. The absorption spectra of 2-StN-NMe_2 (1.5×10^{-5} M) in different solvents. (a) CH_3CN, (b) CF_3CH_2OH, (c) CF_3CH_2OH with 4.5×10^{-3} M triethylamine, (d) CCl_3CH_2OH and (e) CCl_3CH_2OH with 9.0×10^{-3} M triethylamine.



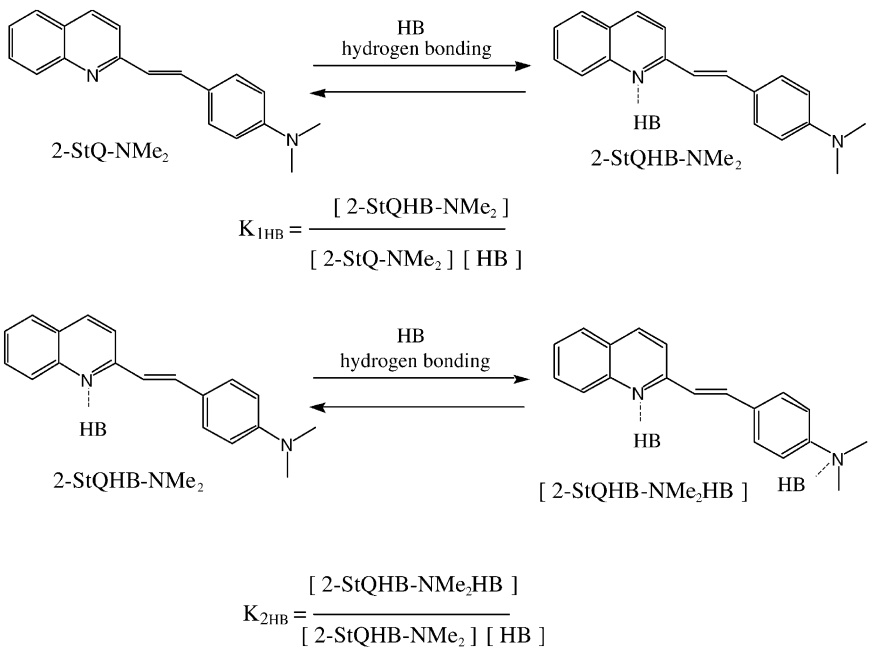
Scheme 1.

concentration of solvent causes a larger shift in absorption maximum. At low TFE content, the complex of HB interaction between 2-StQ-NMe_2 and TFE is more favorable to the mono-HB complex (2-StQHB-NMe_2), and the interaction site is predominant at the more basic site, which is the quinoline group. Since the quinoline group is an acceptor of 2-StQ-NMe_2, the absorption maximum shows a red shift. At high TFE concentration, double HB interaction (2-StQHB-NMe_2HB) is possible in this medium. The HB interaction at the *N*,*N*-dimethylamino site will cause a blue shift in the absorption maximum. Therefore, the shift of the absorption maximum in Table 1 depends on the TFE content. However, the trend in acetonitrile–TCE solution is quite different. The absorption maxima remain red-shifted when the TCE content is increased. From the previous discussion, we conclude that TCE is less possible to form the double HB complex (2-StQHB-NMe_2HB) with 2-StQ-NMe_2 than TFE. We regard the reason is that TCE is larger in molecular size than TFE. For a HB interaction to occur, the interaction sites of two molecules have to be close to each other. The steric effect of HB on the quinoline site is smaller than for the *N*,*N*-dimethylamino site. Therefore, it is easy for TCE and TFE to interact at the quinoline site, and the absorption maximum shows red shift in this situation. Because the interaction of HB has a more sensitive steric effect on the *N*,*N*-dimethylamino site, the HB ability of TFE is much better than TCE at this interaction site because of its smaller molecular size. As indicated in Fig. 1, TFE shows a stronger HB interaction at the *N*,*N*-dimethylamino site than TCE does. TFE causes a larger blue shift in absorption maximum than TCE, by pure HB interaction for 2-StN-NMe_2. For TCE, the HB interaction is predominant at the quinoline site of 2-StQ-NMe_2 and it only shows a red shift in the absorption maximum.

In order to research the steric effect of the HB interaction, we have studied the absorption maxima of 2-StQ-NEt_2 and 2-StN-NEt_2 in which the *N*,*N*-diethylamino group has a greater steric effect than the *N*,*N*-dimethylamino group without changing much of the electron donating ability. The results were compared with 2-StN-NMe_2, and 2-StQ-NMe_2 systems and are listed in Table 2.

Table 1
The absorption maxima of 2-StQ-NMe_2 in different solvents mixed with CH_3CN which include excess triethylamine

v/v_0	Absorption maxima (nm)
[CF_3CH_2OH], 0%	387
[CF_3CH_2OH], 10%	390
[CF_3CH_2OH], 20%	391
[CF_3CH_2OH], 30%	392
[CF_3CH_2OH], 40%	393
[CF_3CH_2OH], 50%	389
[CF_3CH_2OH], 60%	387
[CF_3CH_2OH], 70%	384
Pure CF_3CH_2OH (with triethylamine)	365
[CCl_3CH_2OH], 0%	387
[CCl_3CH_2OH], 5%	389
[CCl_3CH_2OH], 10%	390
[CCl_3CH_2OH], 20%	393
[CCl_3CH_2OH], 40%	397
[CCl_3CH_2OH], 60%	401
[CCl_3CH_2OH], 80%	404
Pure CCl_3CH_2OH (with triethylamine)	406



Scheme 2.

For the 2-StN-NR_2 (R = Me, Et) system, there is only one basic site, the *N*,*N*-dialkylamino group, which can be hydrogen bonded. HB interaction at this site will produce a blue shift in the absorption maximum and solvents with a stronger HB ability will show a larger shift. The shift of absorption maxima in the 2-StQ-NMe_2 system are quite different from the 2-StN-NMe_2 system. The measured red shift in Table 2 is based on the maximum shift from the standard acetonitrile solvent. TCE produce a blue shift in 2-StN-NMe_2 and show a red shift in 2-StQ-NMe_2. TFE produces blue shift in both molecules. The important factors in determining HB ability are steric and electronic effects. For 2-StN-NMe_2, the interaction site is the *N*,*N*-dimethylamino group. This site is sterically more sensitive than the quinoline site. TFE has a strong HB ability and small size. Therefore, it produces a larger blue shift to 2-StN-NMe_2 than TCE. For the 2-StN-NEt_2 system, TFE produce smaller blue shift and TCE does not show any shift at all due to the larger steric effect of the *N*,*N*-diethylamino group.

In 2-StQ-NMe_2, the interaction sites are the *N*,*N*-dimethylamino and quinoline group. The latter is better for HB interaction concerning electronic and steric factors. For solvents which have weak HB ability or large molecular size, the major site for HB in 2-StQ-NMe_2 is the quinoline group. Therefore, TCE produce a red shift in absorption maximum of 2-StQ-NMe_2 because of the HB effect. Only solvents of strong HB ability and small molecular size, such as TFE, can show double HB interaction in 2-StQ-NMe_2 and produce a blue shift in the absorption maximum. There is more steric hindrance at the donor site of 2-StQ-NEt_2. For this compound, it is more difficult for the HB interaction to occur at the *N*,*N*-diethylamino group, and the HB interaction at the quinoline site is more probable than for 2-StQ-NMe_2. Therefore, even TFE cannot produce double HB species with 2-StQ-NEt_2 and only have a red shift in absorption maxima.

To study the HB interaction in the excited states, the emission spectra in different media were measured (Figs. 2 and 3). For the comparison, Fig. 2 indicates the neutral, monoprotonated and doubly protonated spectra of 2-StQ-NMe_2. In pure TFE, the presence of the absorption maximum at 500 nm indicates there is some degree of ground state monoprotonation (Fig. 3a). The emission spectra also show a similar result (Fig. 3a*). The monoprotonated species no longer

Table 2
The absorption maxima of different compounds in different solvents with enough triethylamine

Solvent	2-StN-NMe_2 (nm)	Shift to CH_3CN (cm^{-1})[a]	2-StN-NEt_2 (nm)	Shift to CH_3CN (cm^{-1})[a]	2-StQ-NMe_2 (nm)	Shift to CH_3CN (cm^{-1})[a]	2-StQ-NEt_2 (nm)	Shift to CH_3CN (cm^{-1})a
CH_3CN	363		371		387		398	
CF_3CH_2OH	329	(2847)	340	(2458)	365	(1557)	402	(−250)
CCl_3CH_2OH	340	(1864)	371	(0)	406	(−1209)	422	(−1428)

[a] (+) Blue shift and (−) red shift.

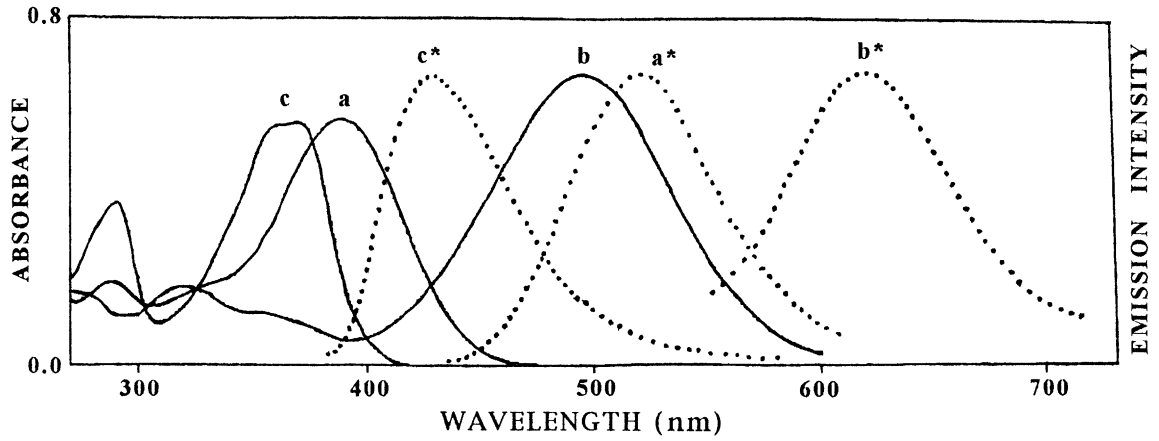


Fig. 2. The absorption and emission spectra of 2-StQ-NMe_2 (1.5×10^{-5} M) in CH_3CN (solid line: absorption, dotted line: emission). (a) Neutral, (b) with 5.0×10^{-5} M HCl, (c) with 1.0×10^{-2} M HCl. (a*) Neutral, EXC = 380 nm; (b*) with 5.0×10^{-5} M HCl, EXC = 500 nm; (c*) with 1.0×10^{-2} M HCl, EXC = 360 nm.

exist in the presence of 2.0×10^{-2} M triethylamine (Fig. 3b). However, we still found a strong emission from the excited state of the monoprotonated species. The reason is that the basicity of quinoline is greatly enhanced in the excited state. Therefore, the ground state HB complexes undergo complete proton transfer upon excitation to give the monoprotonated form (Fig. 3b*) [26–28]. As seen in Fig. 3c, the absorption maxima show that the ground state 2-StQ-NMe_2 exists as a doubly protonated form in pure TCE solvent. The emission spectra (Fig. 3c*) indicated that both the monoprotonated and doubly protonated forms exist in the excited state in this solvent. Thus the excited state deprotonation (ESDP) process occurs at the *N*,*N*-dimethylamino site because the basicity of this site is reduced upon photoexcitation. In the presence of 6.5×10^{-2} M triethylamine, only the ground state HB complex (Fig. 3d) can exist in this condition. However, an excited state proton transfer (ESPT) occurred after photoexcitation, and the emission spectrum of the monoprotonated species was observed as seen in Fig. 3d*.

According to Taft's definition, TFE has a larger δ_c value than TCE, but TCE has higher hydrogen-bond acidity according to Catalán's definition. Thus there are some discrepancies between the definition of hydrogen-bond donor and hydrogen-bond acidity [29–33]. As seen in Fig. 1, our studies have shown that TCE has a greater tendency to cause protonation and create a larger blue shift in the absorption maximum. However, if the influence of protonation could be deleted, TFE is a stronger hydrogen-bond donor than TCE (compared to the extent of blue shift in Fig. 1c and e).

Recently, the singular value decomposition (SVD) method has been proved [34] very useful in the study of solvent–solute association. We will apply the SVD to study the details of our systems in the near future.

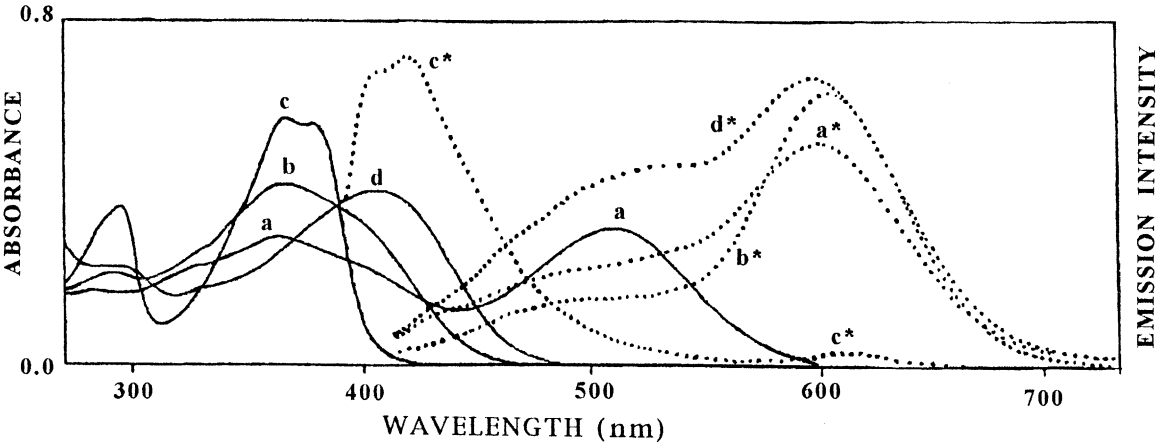


Fig. 3. The absorption and emission spectra of 2-StQ-NMe_2 (1.5×10^{-5} M) in different solvents (solid line: absorption, dotted line: emission, EXC = 380 nm). (a) Pure CF_3CH_2OH, (b) with 2.0×10^{-2} M triethylamine in CF_3CH_2OH, (c) pure CCl_3CH_2OH, (d) with 6.5×10^{-2} M triethylamine in CCl_3CH_2OH. (a*) Pure CF_3CH_2OH, (b*) with 2.0×10^{-2} M triethylamine in CF_3CH_2OH, (c*) pure CCl_3CH_2OH, (d*) with 6.5×10^{-2} M triethylamine in CCl_3CH_2OH.

4. Conclusion

The HB ability of different protic solvents with the ground and excited states of 2-StN-NMe_2, 2-StN-NEt_2, 2-StQ-NMe_2 and 2-StQ-NEt_2 systems was investigated. We could separate the influence between the protonation and pure HB effect on the ICT compound. The steric and ICT effect control the HB interaction of ICT compound. The comparisons of the two strong HB solvents TFE and TCE are most interesting. The ESPT process occurred with the ground state HB complex between 2-StQ-NMe_2 and TFE. The ESDP process was observed for the doubly protonated form of 2-StQ-NMe_2 in TCE. The charge redistribution of the excited ICT systems was applied to explain the ESPT and ESDP processes.

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