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Substituent effects on intramolecular charge-transfer behaviour of styrylheterocycles

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Abstract

To understand the influence of substituents on intramolecular charge transfer (ICT), absorption and emission spectra were measured for several derivatives of 2-styrylquinoline (2-StQ), 2-styrylpyridine (2-StP) and 2-styrylthiophene (2-StT) systems. A strong donor, such as an *N*,*N*-dimethylamino group can produce an ICT compound in these systems, and the excited state dipole moments were measured using a solvatochromic method. Quinoline and pyridine can only act as acceptors. Depending on substituents, the thiophene ring could be a donor or an acceptor. For same donor in our systems, the strength order of different acceptors is quinoline>naphthalene>pyridine>thiophene. Besides electronic effect, steric conformation is also an important factor in ICT molecules. Protonation and hydrogen bonding at acceptor site show red-shift in absorption maxima. The degree of shift depends on the substituents. Interaction at a donor site gives the opposite result. There is a linear relation between excited state dipole moments and absorption energy. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Intramolecular charge transfer; Donor–acceptor interaction; *N*,*N*-dimethylamino group

1. Introduction

Intramolecular charge transfer (ICT) has always been very important in chemistry and biochemistry [1–3]. In the past 30 years, research into donor- and acceptor-containing compounds capable of initiating ICT processes has increased [4,5]. Investigation of ICT molecules focused on systems in which donor and acceptor groups are directly connected through a single bond or π bond [6]. The interaction through single bond focused on through-space interaction between the donor and acceptor [7], and the interaction through π bond concentrated on orbital overlap between donor and acceptor groups [8–10].

The dual fluorescence of dimethylaminobenzonitrile (DMABN) in polar solvents was discovered by Lippert et al., and was attributed to a twisted intramolecular charge transfer (TICT) state [11]. With TICT, two factors are important in predicting the ability to show an excited state charge transfer (CT) character: (i) steric hindrance to planarity [12,13] and (ii) increasing the strength of the donor–acceptor character favors the formation of the TICT state [14].

We have studied the protonation dependent ICT of the styrylquinoline system and have observed a novel deprotonation process in the excited state ICT system [15]. We would like to investigate more about the styrylheterocycles ICT systems in order to understand more about characters of the donor and acceptor [16]. In this work, series of trans-2-styrylquinoline (2-StQ–X), trans-2-styrylpyridine (2-StP–X) and trans-2-styrylthiophene (2-StT–X) derivatives were synthesized and characterized by UV and fluorescence methods. The photophysical behavior of these compounds in various solvents was investigated. The influence of different substituents, hydrogen bonding and protonation was closely examined to characterize the factors of formation of ICT molecules.

2. Experimental

2.1. Materials

Compounds 4-StQ–NMe_2, 4-StP–NMe_2, 2-StQ–X, 2-StP–X and 2-StT–X were prepared by known procedure [17–22]. 4-StQ–NMe_2, 4-StP–NMe_2, 2-StQ–X or 2-StP–X were synthesised by reflux of a mixture of *p*-substituted-benzaldehyde and, either 4-methylquinoline, 4-methylpyri-

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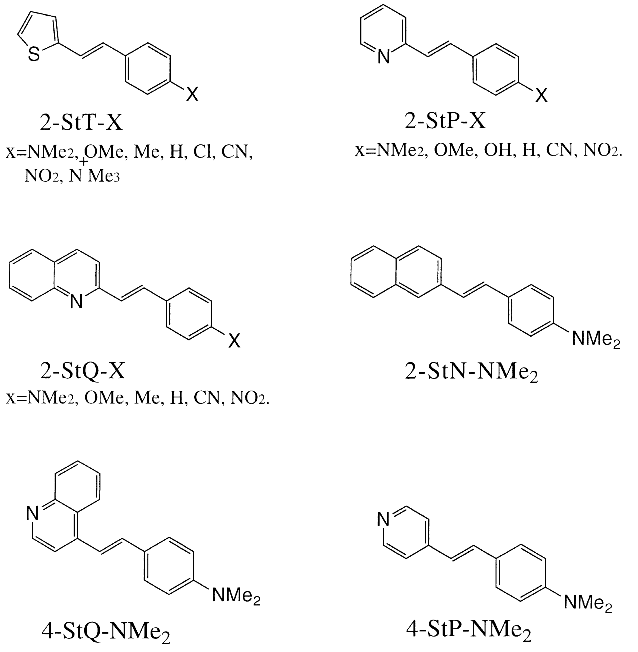

Scheme 1.

dine, quinaldine or 2-methylpyridine, in acetic anhydride for 20 h [23]. The solid product was purified by column chromatography and recrystallized from ethyl acetate. 2-StN–NMe$_2$ and 2-StT–X were prepared by Wittig condensation of *p*-*N*,*N*-dimethylamino-benzaldehyde with 2-methylenenaphathalene or 2-methylenethiophene triethyl phosphonium ylides. The product was recrystallized from benzene. All the solvents were Uvasol grade from Merck or spectrophotometric grade from ACROS and were used as received. 2-StT–N$^+$Me$_3$ was obtained from reacting a mixture of 2-StT–NMe$_2$ and CH$_3$I in toluene for 48 h. The melting points were as follows: 2-StN–NMe$_2$, 195–196°C; 2-StT–NMe$_2$, 146–148°C; 2-StT–OMe, 134–135°C (lit. 135–137°C) [20]; 2-StT–Me, 116–117°C; 2-StT–H, 107–109°C (lit. 113–115°C) [22]; 2-StT–Cl, 133–134°C; 2-StT–CN, 148–149°C, 2-StT–NO$_2$, 177–178°C (lit. 174°C) [21]; 2-StT–N$^+$Me$_3$, dec. 192°C; 4-StQ–NMe$_2$, 143–144°C; 2-StQ–NMe$_2$, 186–187°C (lit. 184–185°C) [17]; 2-StQ–OMe, 123–125°C (lit. 125–126°C) [18]; 2-StQ–OH, 127–128°C; 2-StQ–H, 96–97°C (lit. 98–100°C) [18]; 2-StQ–CN, 146–147°C (lit. 154°C) [19]; 2-StQ–NO$_2$, 166–168°C; 4-StP–NMe$_2$, 244–246°C (lit. 241°C) [20]; 2-StP–NMe$_2$, 140–141°C (lit. 139°C) [20]; 2-StP–OMe, 69–71°C (lit. 69°C) [20], 2-StP–H, 87–88°C; 2-StP–CN, 125–127°C (lit. 123–124°C) [19]; 2-StP–NO$_2$, 131–134°C; 2-StP–Me, 80–82°C. The structure of styrylheterocycles were shown in Scheme 1.

2.2. Method

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

Table 1
The absorption and emission maxima (nm) of 2-StQ–X in methanol (EXC=330 nm)

Substitutent	Absorption maxima		Emission maxima
	Neutral	Acidic with HCl	
–O$^-$	398		589
–NMe$_2$	395	503	547
–OMe	347	408	437
–OH	338	395	388
–H	338	378	380
–CN	338	363	380
–NO$_2$	351	365	No

3. Results

3.1. 2-Styrylquinoline system

The absorption and emission maxima of different derivatives of 2-styrylquinolines (2-StQ–X) in methanol solvent are recorded (Table 1). The electron-donating substituents at the para position of the benzene ring have caused the red-shift of the absorption maxima. Thus, compound 2-StQ–H shows an absorption maximum at 338 nm which compares with the absorption maximum of 347 nm from compound 2-StQ–OMe.

The derivative with the strongest electron-donating group (2-StQ–NMe$_2$) shows the largest red-shift, at 395 nm, and its fine structure disappears at shorter wavelengths. This new absorption band can be assigned as the ICT band. For lesser electron-donating groups, such as the hydroxy derivative, the absorption maximum is similar to the hydrogen substitutent (2-StQ–H). The absorption maximum for compound 2-StQ–OH under basic conditions also has a red-shift to about 398 nm, even longer than the 395 nm in compound 2-StQ–NMe$_2$. Under basic conditions, the hydroxy group is deprotonated and becomes a phenoxide anion. From the red-shift of the absorption maxima, it can be seen that phenoxide anion substituent has a stronger ICT effect than the *N*,*N*-dimethylamino group.

The electron-withdrawing substituents at the para position of the benzene ring show similar effects on the absorption spectra. Compared to 2-StQ–H, the absorption maximum of 2-StQ–CN is similar but the fine structure disappears. The red-shift of compound 2-StQ–NO$_2$ is more obvious (Table 1).

The fluorescence spectra of the styrylquinoline derivatives are shown in Fig. 1. The red-shift of the emission maxima are more obvious than the absorption maxima. The phenoxide ion substituent causes largest shift to 589 nm (compared to 380 nm for the hydrogen substituent in Table 1). The hydroxy

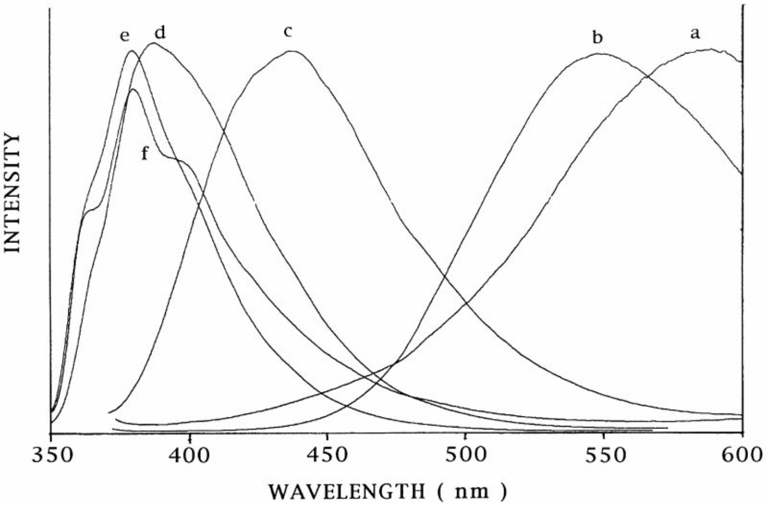

Fig. 1. The emission spectra of 2-StQ–X in methanol (EXC=330 nm): (a) –O^-; (b) –NMe_2; (c) –OMe; (d) –OH; (e) –H and (f) –CN.

substituent shows the smallest red-shift. There is no shift for the cyano substituent, and no emission is observed for the nitro substituent.

There is also a solvent effect on the emission maxima of the styrylquinoline derivatives, with the dimethylamino group exhibiting the largest effect. From the solvent effect, the excited dipole moment (19 D) was obtained for the compound 2-StQ–NMe_2 [15]. The solvatochromic effect on the emission spectra for the methoxy derivatives is also observable, but is less obvious in the hydroxy derivatives. The emission spectra of the electron-withdrawing substituents, such as the cyano derivatives, even show fine structure in methanol solvent. Since the nitrogen atom in the quinoline ring is capable of receiving protons from the protic acid, the styrylquinoline systems become protonated species in high medium acidity. The absorption maxima of the protonated styrylquinoline derivatives are listed in Table 1. By comparsion with the non-protonated derivatives, we found that the absorption maxima of the protonated styrylquinoline derivatives had red-shift. The extent of red-shift in absorption maxima is proportional to the electron-donating ability at the para position of the benzene ring.

3.2. 2-Styrylpyridine system [24]

The absorption maxima of 2-StP derivatives are recorded in Table 2. Both electron-donating and electron-withdrawing substituents cause red-shift in absorption maxima, and the extent of red-shift is proportional to the donating or withdrawing ability of the substituents [25]. The appearance of red-shift is also accompanied by the disappearance of fine structure in the absorption spectra. The absorption maximum of the nitro substituent (2-StP–NO_2) is located at 335 nm while that for the hydrogen substituent (2-StP–H) is at 306 nm. The extent of red-shift caused by the electron-withdrawing group is larger than for the 2-StQ system. The emission spectra of the styrylpyridine derivatives are shown in Fig. 2. Compared to the emission maximum of 2-StP–H at 360 nm, the emission maximum of 2-StP–NMe_2 is red-shifted to 488 nm. This red-shift value of 7286 cm^{-1} is not as large as the corresponding shift of 8035 cm^{-1} in styrylquinoline systems (Table 1, 380 nm for X=H versus 547 nm for X=NMe_2). The styrylpyridine derivatives also have a basic nitrogen atom on the pyridine ring, thus, 2-StP–X are capable of protonation in the presence of suitable protic acids. The absorption and emission maxima of the protonated styrylpyridine derivatives are all red-shifted, and the extent of red-shift is proportional to the electron-donating ability of substituents. The nitro derivative (2-StP–NO_2) showed the least red-shift in the absorption maxima upon protonation (from 335 to 337 nm).

3.3. 2-Styrylthiophene system

The absorption and emission spectra of 2-StT derivatives (2-StT–X) are shown in Figs. 3 and 4, respectively, and the absorption and emission maxima in methanol are summarized in Table 3. The absorption maxima show red-shift when the electron-donating or electron-withdrawing ability

Table 2
The absorption and emission maxima (nm) of 2-StP–X in methanol (EXC=310 nm)

Substitutent	Absorption maxima		Emission maxima (neutral)
	Neutral	Acidic with HCl	
–NMe_2	368	447(mono), 324(double)	488
–OMe	336	376	402
–Me	314	349	373
–H	306	341	360
–CN	318	330	364
–NO_2	335	337	No

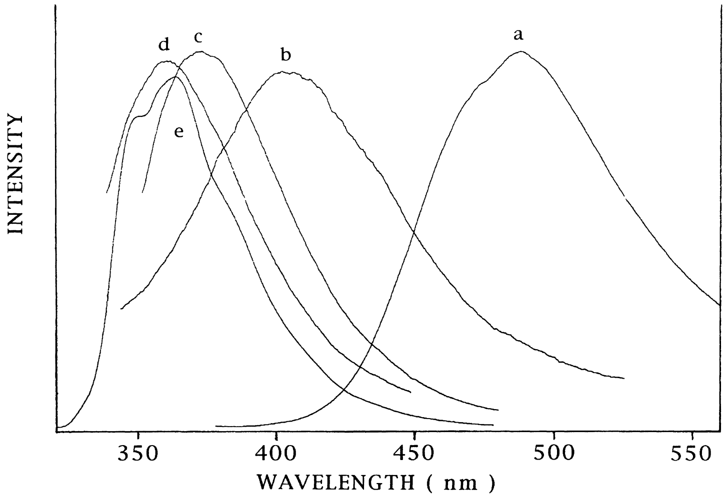

Fig. 2. The emission spectra of 2-StP–X in methanol (EXC=310 nm): (a) –NMe$_2$; (b) –OMe; (c) –Me; (d) –H and (e) –CN.

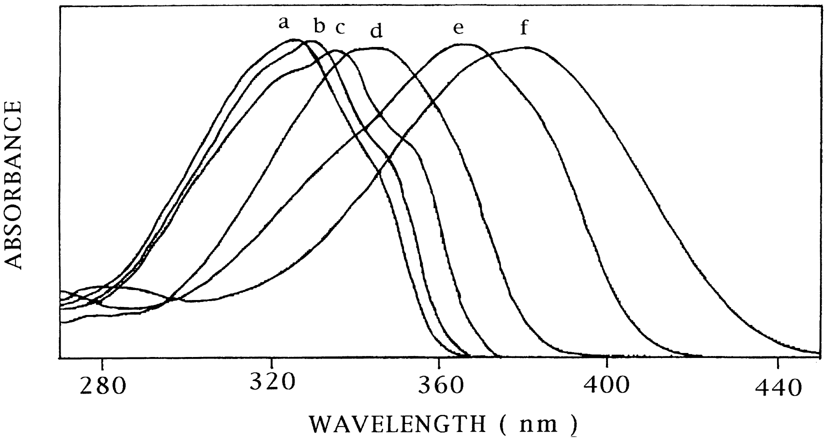

Fig. 3. The normalized absorption spectra of 2-StT–X in chloroform: (a) –H; (b) –Me; (c) –OMe; (d) –CN; (e) –NMe$_2$ and (f) –NO$_2$.

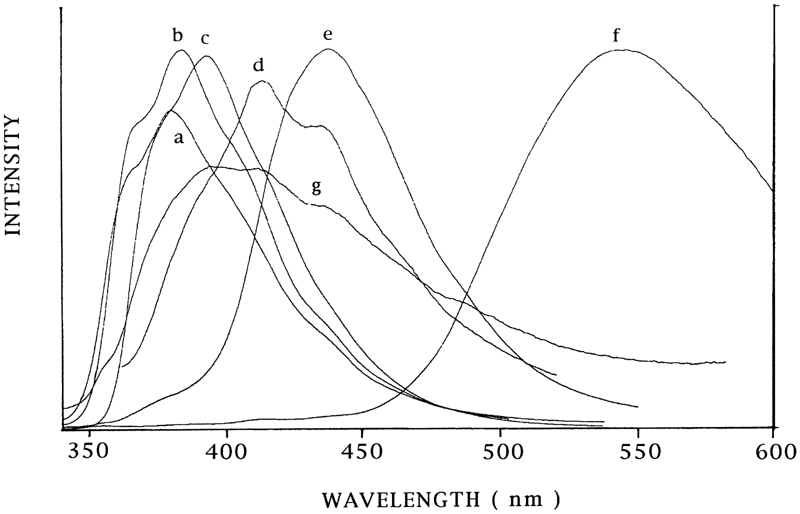

Fig. 4. The emission spectra of 2-StT–X in chloroform (EXC=320 nm): (a) –H; (b) –Me; (c) –OMe; (d) –CN; (e) –NMe$_2$; (f) –NO$_2$; (g) –NMe$_2$ and acidic with CF$_3$COOH.

Table 3
The absorption and emission maxima (nm) of 2-StT–X in methanol (EXC=310 nm)

Substitutent	Absorption maxima	Emission maxima
–NMe_2	358.0, 234.0 (324.5)[a]	450
–N^+Me_3	327	
–OMe	331.0	386
–Me	325.0	378
–H	321.0	375
–CN	338.0	415
–NO_2	370.0	No

[a] Acidic with HCl.

of substituents increased. Unlike the styrylpyridine and styrylquinoline systems, the absorption spectrum of the methoxy derivative (2-StT–OMe) still shows fine structure, and the absorption spectrum of the nitro derivative (2-StT–NO_2) even shifted to longer wavelength than the *N*,*N*-dimethyl amino derivative (2-StT–NMe_2). In order to obtain the extent of charge separation in the ground and excited states, the solvatochromic effect on the chromophore was studied using the following equations [26]:

$$u_A - u_F = m_1 f(\varepsilon, n) + \text{constant} \tag{1}$$

$$u_A + u_F = -m_2[f(\varepsilon, n) + 2g(n)] + \text{constant} \tag{2}$$

where

$$m_1 = \frac{(\mu_e - \mu_g)^2}{ba^3} \tag{3}$$

$$m_2 = \frac{\mu_e^2 - \mu_g^2}{ba^3}, \quad b = 2\pi\varepsilon_0 hc = 1.105 \times 10^{-35}, \quad c = \text{constant} \tag{4}$$

If the molecule is considered as spherical and isotropically polarizable then *f*(ε, n) and *g*(n) functions are defined in Eqs. (5) and (6), respectively.

$$f(\varepsilon, n) = \left(\frac{2n^2+1}{n^2+2}\right)\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) \tag{5}$$

$$g(n) = \frac{2}{3}\left[\frac{n^4-1}{(n^2+2)^2}\right] \tag{6}$$

where n and ε are the refractive index and dielectric constants, respecyively, of a particular solvent, u_A and u_F the absorption and emission maxima (cm^{-1}), 'a' the radius of the molecule, μ_g and μ_e are the ground and excited state dipole moments.

The calculated dipole moments of the ground and excited states are listed in Table 4. The strong electron-donating substituents, such as the dimethylamino group, show a relatively large excited state charge separation (excited state dipole moment) in all the styrylquinoline, styrylpyridine and styrylthiophene systems. The styrylquinoline systems have the largest excited dipole moments. It was also found that the donating effect in the quinoline ring is stronger at the 4-position than at the 2-position. Only in styrylquinoline and styrylpyridine systems could methoxy substituent produce a relatively large excited dipole moment; it could not happen in styrylthiophene system. For the electron-withdrawing

Table 4
The absorption and emission maxima, ground state and excited state dipole moment of different compounds

Compound	a[a] (Å)	μ_g (D)	μ_e (D)	Ionic[b] (%) excited state	Absorption[c] (nm)	Emission[c] (nm)	Absorption (ε)[d] (nm)
2-StN–NMe_2[e]	8	3	15	20	363	485	357 (27600)
4-StP–NMe_2	7	4	14	21	369	488	375 (32000) 250 (14400)
4-StQ–NMe_2	8	5	27	35	392	551	402 (14100)
2-StP–NMe_2	7	2	13	19	363	473	368 (29600) 249 (7700)
2-StQ–NMe_2	8	4	19	24	387	538	395 (35800) 290 (11200) 254 (16900)
2-StT–NMe_2	7	3	12	17	363	455	358 (29400)
2-StP–OMe	7	1	11	16	320	404	336 (25200)
2-StQ–OMe	8	0	14	18	355	437	347 (27300) 291 (18500)
2-StT–OMe	7	2	3	4	332	386	331 (27900)
2-StT–H	6	1	2	3	322	379	321 (29200)
2-StT–Cl	6	1	3	5	326	387	326 (29900)
2-StT–CN	6.5	3	8	12	338	424	338 (30100)
2-StT–NO_2	6.5	2	13	21	372	588	370 (24300)

[a] Onsager radius.
[b] Ionic (%) of excited state was obtained by [$\mu_e \times 100\%$]/[$2a \times 4.8$ D].
[c] In acetonitrile.
[d] $\varepsilon = cm^{-1}\,mol^{-1}\,l$, in methanol.
[e] 2-StN–NMe_2: *p*-*N*,*N*-dimethylamino-2-styrylnaphthalene.

groups, such as cyano and nitro groups, a relatively large charge separation was produced in the styrylthiophene system. However, this is impossible in styrylquinoline and styrylpyridine systems.

4. Discussion

4.1. Excited state dipole moment

For 2-StQ–NMe$_2$, there are two basic nitrogen atoms, at the quinoline and *N*,*N*-dimethylamino sites. The pK_a values of quinoline and *N*,*N*-dimethylaniline are 4.90 and 5.15, respectively [27]. For the individual molecules, *N*,*N*-dimethylaniline is a stronger base than quinoline. In 2-StQ–NMe$_2$, there is ground state CT from the *N*,*N*-dimethylamino to the quinoline site. This is through the rotation of the *N*,*N*-dimethylamino C–N bond where the lone pair electrons of the nitrogen atom are in parallel with the π-ring electrons. Thus, the *N*,*N*-dimethylamino group becomes a strong electron donor to the ICT system and this is a general rule for the donor–acceptor interaction. For quinoline, the lone pair electrons of the nitrogen atom are in an orbital which is perpendicular to the π-ring system, and it is difficult for this nitrogen to become a donor through the resonance effect. Also, nitrogen is more electro-negative than carbon atom and this makes quinoline act only as an acceptor in the ICT interaction. Thus, in 2-StQ–NMe$_2$, the ground state ICT interaction makes the *N*,*N*-dimethylamino group less basic than quinoline; the pK_a values are 2.82 and 5.95, respectively [15], and the quinoline system become more basic. In the excited states, the pK_a values can be obtained by the Forster cycle equation (Eq. (7))

$$\mathrm{p}K(S_0) = \mathrm{p}K(S_1) + 2.1 \times 10^{-3}\,\Delta\nu\ (\text{at } 298\,\mathrm{K}) \qquad (7)$$

where S_0, S_1 are ground and excited state, and $\Delta\nu$ is defined as the excitation energy difference (cm^{-1}) between protonated and non-protonated species [28]. In 2-StQ–NMe$_2$, the pK_a values of excited state in the *N*,*N*-dimethylamino and quinoline group are -12.2 and 17.4, respectively [15].

It is understandable that more charge separation occurred in this ICT excited state. Since quinoline is an acceptor, as the electron-donating ability of the substituent become weaker, the ICT also becomes less pronounced. The excited state dipole moment of the methoxy derivative (2-StQ–OMe) is 14 D and the hydroxy derivative (2-StQ–OH) even has fine structure in the emission spectrum. It is difficult to calculate the excited dipole moment of 2-StQ–OH.

The situation of styrylpyridine systems is similar to the styrylquinoline systems. The lone pair electrons of the pyridine nitrogen are in an orbital perpendicular to the aromatic electron system. It is also difficult for pyridine to act as donor. As an acceptor, pyridine is less efficient than quinoline. Thus, with the same electron-donating group, the styrylpyridine derivatives have less charge separation in the excited state (Table 4).

By comparing the extent of charge separation in the excited states of *N*,*N*-dimethylamino derivatives of styrylnaphthalene (2-StN–NMe$_2$), styrylquinoline (2-StQ–NMe$_2$), styrylpyridine (2-StP–NMe$_2$) and styrylthiophene (2-StT–NMe$_2$), it was found that quinoline is a better acceptor than naphthalene (excited charge separation of 24% versus 20%). The thiophene moiety is the worst acceptor with an excited state charge separation of only 17% in 2-StT–NMe$_2$. In fact, one of the lone pair electrons of the sulfur atom in the thiophene ring is capable of resonancing into the thiophene ring to achieve aromaticity. This means the thiophene ring could act as a donor. The excited dipole moment of 2-StT–NMe$_2$ is only 12 D which is the smallest among the dimethylamino derivatives. The excited dipole moments of 2-StT–OMe and 2-StT–H decreased to 3 and 2 D, respectively. However, when the electron-withdrawing ability of the substituent increased, the excited dipole moment increase from 3 D (2-StT–Cl) to 8 D (2-StT–CN) and finally to 13 D (2-StT–NO$_2$). Thus, it is reasonable that reverse ICT occurred when the electron-withdrawing ability of the substituent increased, and thiophene moiety become the electron donor.

4.2. The excited dipole moments and the absorption energies

In the styrylthiophene system, there is a linear relationship between the excited state dipole moments and the absorption maxima (in methanol) (Fig. 5). We regard that the stabilization in the excited state by polar solvent depends on the extent of excited state dipole moments. The more ground state dipole moment may lead to bigger dipole moment in the localized excited state. If the excited state is more stabilized, the energy to promote its electronic state become lower, so the lower absorption energy was mea-

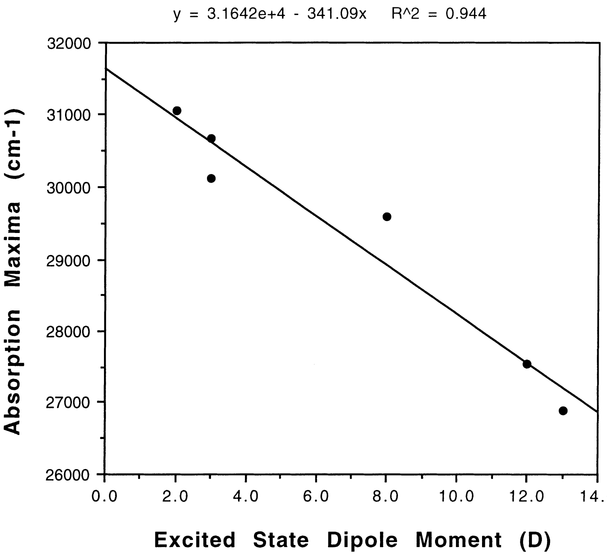

Fig. 5. The relation on absorption maxima and excited state dipole moment in 2-StT–X system.

sured. Thus, the larger excited dipole moments correspond to greater red-shift in the absorption maxima.

The excited dipole moments are obtained by measuring the absorption and emission maxima of the molecule in different solvents. If the molecule is not fluorescent, as in the case of most nitro derivatives, it is difficult to obtain the excited dipole moments. However, we can use an absorption energy in methanol versus excited dipole moment plot (Fig. 5) to evaluate the approximate excited dipole moment for the non-fluorescent molecules.

4.3. *The effects of protonation and hydrogen-bonding on the spectroscopic behavior*

If we compare the absorption maxima of different molecules in acetonitrile and methanol (Table 4), molecules can be divided into three categories. Considering the solvent effects on the absorption maxima (1) there is almost no change in these two solvents, such as for all the styrylthiophene derivatives except 2-StT–NMe$_2$; (2) the absorption maxima had a red-shift between acetonitrile and methanol, which includes all the *N*,*N*-dimethylamino derivatives except 2-StT–NMe$_2$ and 2-StN–NMe$_2$ and (3) a blue-shift occurs between acetonitrile and methanol, as in the cases of 2-StN–NMe$_2$, 2-StT–NMe$_2$ and 2-StQ–OMe.

The hydrogen bonding effects on the acceptor or donor obviously show different effects. In acetonitrile, there is little or no hydrogen bonding between solvent and chromophore. In methanol, the basic nitrogen atoms of the 2-StQ–X and 2-StP–X systems are hydrogen bonding with solvent. When the acceptor is hydrogen-bonded, a more charge-separated chromophore is more stabilized. The stabilization effect from the hydrogen bonding is even larger in the excited states, and thus, shows red-shift in the absorption maxima. If the hydrogen bonding is on the donor site of the ICT system, such as an *N*,*N*-dimethylamino nitrogen, the charge of the excited state at this site becomes weaker, and thus, causes the blue-shift [29]. In the styrylthiophene systems, there is no hydrogen bonding at either the donor or acceptor sites and therefore no change in the absorption maxima.

In the presence of enough protic acid, 2-StQ–X and 2-StP–X systems protonate at the acceptor site. In an ICT molecule, the basicity of an acceptor will increase in the excited state and the protonated chromophore is stabilized by solvent molecules. Thus, the absorption maximum shows a red-shift. If the donor site of the ICT molecule is protonated, the absorption maxima will show blue-shift. The extent of the shift depends on the extent of the excited state charge separation. In the 2-StQ–X system, when the electron-donating ability decreases, the excited state charge separation and the red-shift of a protonated species in the absorption maximum decreases. Thus, 2-StQ–NMe$_2$ shows the largest shift with 5436 cm^{-1} and 2-StQ–NO$_2$ has only an 1093 cm^{-1} shift after protonation (Table 1). For the 2-StP–X system, since pyridine is a weaker electron-acceptor, the protonated form shows less red-shift. There is almost no red-shift in 2-StP–NO$_2$. For all the styrylquinoline and styrylpyridine systems, protonation can only show red-shift. Thus, the pyridine and quinoline rings act only as electron-acceptors.

4.4. *Reverse charge transfer*

Depending on competitors, many aromatic group can act as an electron-donor or acceptor. For example, research on trans-9-anthracene and trans-1-naphthalene by Gorner and co-workers [30,31], polyene by Johnson et al. [32] and phenyl, 1-naphthalene and 9-anthracene by Sinha and Yate [33] all indicate that these compounds can act as electron-donors. Comparison with the phenyl and naphthalene groups suggests that the reason pyridine and quinoline group cannot act as electron-donors is the higher electro-negativity of the nitrogen atom in the pyridine and quinoline rings. In the 2-StT–X system, if the substituent is an electron-donating group, the thiophene ring acts as an electron-acceptor.

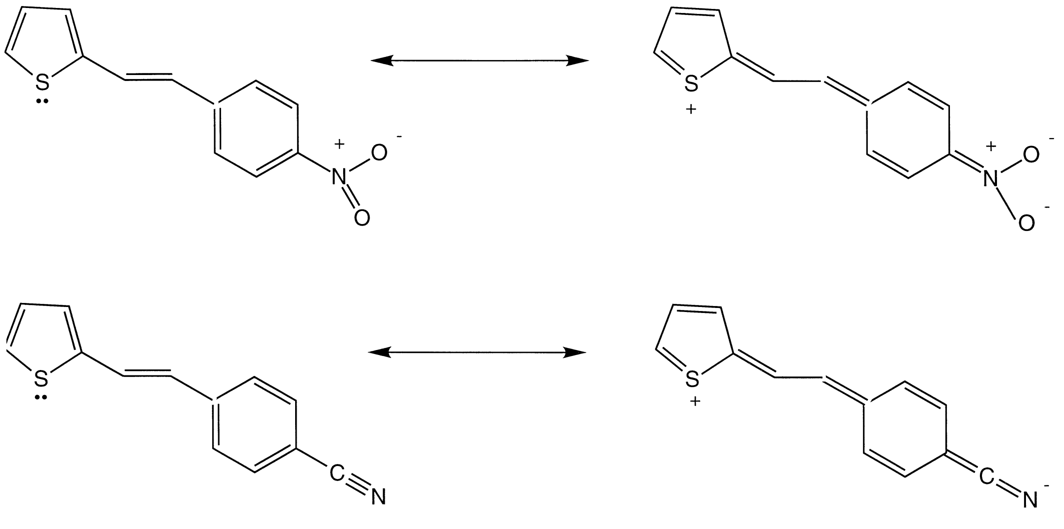

Fig. 6. The resonance forms of 2-StT–NO$_2$ and 2-StT–CN.

When the substituent is a strong electron-withdrawing group, the thiophene moiety becomes a donor instead [34]. The electron-withdrawing ability of the quaternary nitrogen and protonated *N*,*N*-dimethylamino groups is stronger than that of the cyano and nitro groups. In the 2-StT–X system, the weaker electron-withdrawing groups, such as cyano and nitro, can act as electron-acceptors, but the quaternary nitrogen and protonated *N*,*N*-dimethylamino groups show quite different behavior.

Since 2-StT–N^+HMe_2 and 2-StT–N^+Me_3 are salts and are hard to dissolve in nonpolar solvents, it is difficult to obtain the excited dipole moment by the solvatochromic method. However, we can use the linear relation between the absorption energy and dipole moments (Fig. 5) to estimate the excited dipole moment of 2-StT–N^+HMe_2 and 2-StT–N^+Me_3. From Table 3, we know that the absorption maxima of 2-StT–N^+HMe_2 and 2-StT–N^+Me_3 were shifted to 324.5 and 327 nm, respectively, which indicates no ICT behavior.

Why can the –N^+HMe_2 and –N^+Me_3 groups, such as those in 2-StT–N^+HMe_2 and 2-StT–N^+Me_3, not act as electron-acceptors in the ICT system? It has been concluded that an excited twisted conformation is necessary for the ICT phenomenon to occur in nitro-aromatic compounds [33]. The –N^+HMe_2 and –N^+Me_3 substituents cannot become twisted with parent molecule such as the –NMe_2 group in 2-StT–NMe_2 or the –NO_2 group in 2-StT–NO_2. In addition, the –N^+HMe_2 and –N^+Me_3 groups cannot participate in a resonance form, such as the 2-StT–NO_2 and 2-StT–CN depicted in Fig. 6. If one draws a resonance form of 2-StT–N^+HMe_2, then it will result in a deprotonation process. Thus, even though the –N^+HMe_2 and –N^+Me_3 groups are strong electron-withdrawing groups, the ICT phenomenon does not occur in either 2-StT–N^+HMe_2 or the 2-StT–N^+Me_3 molecule.

5. Conclusion

The influence of substituents on the electronic spectrum have been shown in different systems. For different aromatic systems, a CT band was observed for strong electron-donating substitutents such as an *N*,*N*-dimethylamino group. For the same donor group, the order of acceptor strength is quinoline>naphthalene>pyridine>thiophene. Strong withdrawing groups such as the nitro group only show a CT absorption band in 2-StT–X systems. In our research, quinoline and pyridine rings only behave as acceptors in the styryl system. Depending on the competitor, a thiophene ring can become a donor or an acceptor. Beside the influence of electronic density, another important factor in the ICT phenomenon is the conformation effect. In 2-StT–X systems, only –CN and –NO_2 groups show a CT absorption band. For 2-StT–N^+Me_3 and 2-StT–N^+HMe_2, only fine structure was observed.

An ICT molecule changes its electronic density distribution after photo-excitation. In ICT systems, the basicity of an acceptor decreases after photo-excitation. Protonation and hydrogen bonding at this site have red-shift in the absorption maximum. The degree of shift depends on the excited state dipole moment. If protonation and hydrogen bonding occur in the donor, the tendency is for the absorption maximum to shift in the opposite direction. There is a linear relation between absorption energy and excited state dipole moments, with larger dipole moments requiring lower energies.

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