Styrylpyridine–amine exciplexes: substituent effects

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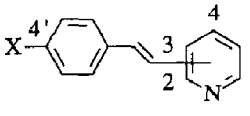
(Received September 7, 1993; accepted March 24, 1994)

Abstract

Fluorescent exciplexes were observed between excited para-substituted *trans*-styrylpyridines (*n*-StP, $n=2,3,4$ and X ≡ CN, Cl, H, $(CH_3)_2CH$, CH_3, CH_3O) and three tertiary amines, (*i.e.* diisopropyl ethylamine, tributylamine and triethylamine) in *n*-hexane at room temperature. The exciplex emission for the 2-StP–amine system was extremely weak. The maximum fluorescence energies were correlated with the values of Rehm and Weller, except for those for the StP with cyano groups. There was better correlation when a stronger electron-donating amine was used. The quenching rate constants increase as ΔG^0 for electron transfer becomes more exergonic, except for the case of cyano derivatives. The exciplex fluorescent energies also showed a linear correlation with the Hammett σ_p constants, again except for the cyano derivatives. The calculated dipole moments for the styrylpyridine–amine exciplexes are larger than those for stilbene–amine exciplex systems.

1. Introduction

Trans-styrylpyridines (*n*-StP, $n=2,3,4$) are similar to *trans*-stilbene in structure, except one carbon atom at position 2, 3 or 4 was replaced by nitrogen atoms. This simple replacement causes various complicated changes in photochemical and photophysical properties [1–4]. However, the presence of an (n, π^*) state does not seem to change the isomerization mechanism of *n*-StP, except at very low temperature [1], when the triplet manifold became more important.



4'-X-*n*-StP, $n = 2, 3, 4$

X ≡
1 CN
2 Cl
3 H
4 CH_3
5 $(CH_3)_2CH$
6 CH_3O

Scheme 1.

We have studied the substituent effect on the exciplex behaviors of *trans*-stilbene–amine [5] and phenanthrene–olefine [6] systems. The exciplex fluorescence energies could be tuned by varying substituents at excited donors or acceptors. We are interested in studying the effect of substituents on *n*-StP–amine systems, so prepared the following *n*-StP with substituents at position 4 of the phenyl moiety. We wish to report the exciplex behavior for *n*-StP (Scheme 1, **1–6**) (with $n=2,3,4$) with tertiary amines such as diisopropylethylamine (DIPEA), triethylamine (TEA) and tributylamine (TBA).

2. Experimental details

The para-substituted *n*-StP specimens (**1–6**) were prepared from para-substituted benzaldehyde and *n*-pyridylmethyl foramide by Wittig reactions [7]. The products were purified by column chromatography and recrystallization. The melting points were as follows: 2-StP(**1**), 125–127 °C; 2-StP(**2**), 78–79 °C; 2-StP(**3**), 87–88 °C; 2-StP(**4**), 80–82 °C; 2-StP(**5**), 48–50 °C; 2-StP(**6**), 69–71 °C; 3-StP(**1**), 98–99 °C; 3-StP(**2**), 80–81 °C; 3-StP(**3**), 79–80 °C; 3-StP(**4**), 105–106 °C; 3-StP(**5**), 63–65 °C; 3-StP(**6**), 100–101 °C; 4-StP(**2**), 108–110 °C; 4-StP(**3**), 127–128 °C; 4-StP(**4**), 149–150 °C; 4-StP(**5**), 100–102 °C; 4-StP(**6**), 129–131 °C.

The TEA, DIPEA and TBA were of reagent grade (Merck) and were purified by distillation over a base. The solvents used for the fluorescence and lifetime measurements were of spectroscopic grade (Merck).

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SSDI 1010-6030(94)03855-O

Fluorescence spectra were recorded using a Perking–Elmer LS-5 luminescence spectrometer. Fluorescence quenching data were obtained from degassed solutions containing less than 10^{-4} M StP and various concentrations of amine quencher. The oxidation potentials (in volts *vs.* Ag/saturated silver chloride electrode) were measured on a cyclic voltmeter (EG&G Princeton applied research, model 173, potentiostat/Galvanostat and model 175 Universal programmer) in polar aprotic solvent (acetonitrile) with a glass–carbon disc as the working electrode and tetraethylammonium perchlorate (0.1 M) as the supporting electrolyte.

3. Result

The substituent and nitrogen positions have little effect on the absorption and emission maxima for the para-substituted styrylpyridines (*n*-StP **1**–*n*-StP **6**). The 0,0 transition energies $E_{0,0}$ for the styrylpyridines were calculated from the absorption and emission maxima, and are listed in Table 1 along with the absorption and emission maxima.

The fluorescence of the para-substituted styrylpyridine (2-StP, 3-StP and 4-StP with substituent **1**–**6**) can all be quenched by tertiary amines in *n*-hexane. The Stern–Volmer quenching constant can be obtained by varying the quencher concentrations. The quenching constants (K_{sv}) thus obtained for TEA, TBA and DIPEA in *n*-hexane are listed in Table 2.

TABLE 1. Absorption and emission maxima of para-substituted 4′-X-2,3,4-StP, and the singlet excitation energies

	λ_{max}^{fluo} (nm)	λ_{max}^{UV} (nm)	$E_{0,0}$ (eV)
4′-X-2-StP			
CN	363.5	319	3.65
Cl	360.5	316	3.68
H	356	313	3.72
Me	363	319	3.66
Isopropyl	362.5	320	3.65
MeO	371.5	326	3.57
4′-X-3-StP			
CN	359	312	3.72
Cl	358.8	303	3.78
H	354	303	3.80
Me	360	308	3.74
Isopropyl	359.3	307	3.75
MeO	369.5	320	3.62
4′-X-4-StP			
CN	368	307	3.71
Cl	352	298	3.84
H	346	291	3.92
Me	355	311	3.74
Isopropyl	354	311	3.75
MeO	369	321	3.61

TABLE 2. Stern–Volmer quenching constant (K_{sv}, M^{-1}) of 4′-X-2,3,4-StP and quenching rate constant k_q of 4′-X-3-StP quenched by three different tertiary amines

	K_{sv} (M^{-1})			$k_q \times 10^{-10}$		
	DIPEA	TBA	TEA	DIPEA	TBA	TEA
4′-X-2-StP						
CN	4.54	2.84	3.29			
Cl	1.01	0.52	0.53			
H	0.51	0.29	0.31			
Isopropyl	0.50	0.24	0.30			
Me	0.52	0.33	0.26			
MeO	0.37	0.11	0.19			
4′-X-3-StP						
CN	5.00	3.87	3.92	0.50	0.39	0.39
Cl	12.0	8.90	8.50	2.63	1.86	1.86
H	9.70	6.32	6.85	1.07	0.76	0.76
Isopropyl	5.00	3.96	4.20	0.30	0.23	0.12
Me	5.50	4.01	3.43	0.55	0.40	0.35
MeO	2.00	1.21	0.63	0.20	0.12	0.06
4′-X-4-StP						
CN	54	30	33			
Cl	2.68	2.00	1.85			
H	2.29	0.86	0.94			
Isopropyl	1.08	0.71	1.00			
Me	2.20	1.14	0.57			
MeO	0.77	0.64	0.49			

When the quencher concentration increased, structureless and red-shifted exciplex emissions were observed. The exciplex fluorescences for the 4-styrylpyridines–DIPEA (Fig. 1(a)) and 3-styrylpyridines-DIPEA (Fig. 1(b)) are shown along with the monomer fluorescence. The exciplex fluorescent maxima in *n*-hexane are shown in Table 3. The exciplex emission for the 2-styrylpyridines–amine system was so weak that it was difficult to record the maxima emissions. The exciplex fluorescent maxima exhibit increasing red shift and decreasing intensity when solvent polarity is increased.

The dipole moment of the exciplex can be estimated from the variation of the exciplex emission maxima ν_{max} with solvent polarity $f(n,\epsilon)$ [8], as described by

$$\nu_{max} = \nu_0 - 2\left(\frac{\mu^2}{hca^3}\right)\left\{\frac{(\epsilon-1)}{(2\epsilon+1)} - \frac{(n^2+1)}{(4n^2+2)}\right\} \quad (1)$$

Here, ν_0 denotes the hypothetical gas phase emission frequency, μ is the dipole moment, a is the solvent cavity radius (approximately 4.5 Å), h is the Planck constant, n is the refraction index and ϵ is the dielectric constant of the solvent. From the linear plot of ν_{max} *vs.* the polarity of the solvent

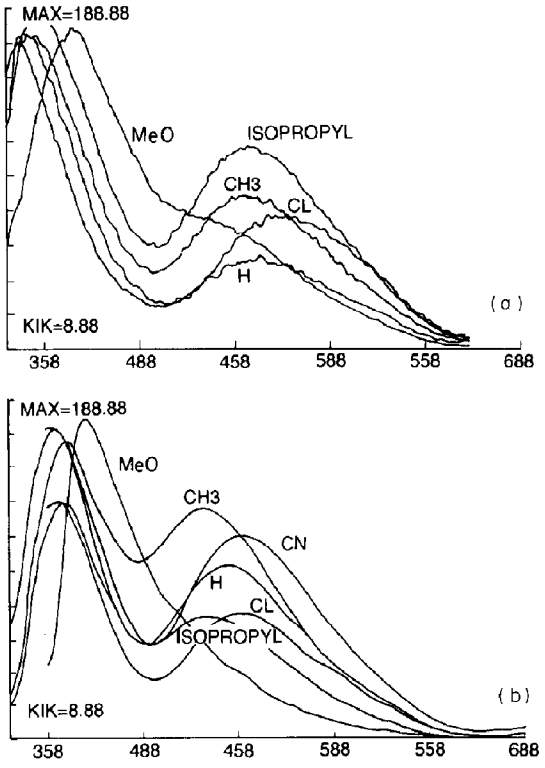

Fig. 1. Exciplex spectra of (a) 4′-X-4-StP–DIPEA and (b) 4′-X-3-StP–DIPEA exciplex systems in *n*-hexane at 298 K.

(Fig. 2), the dipole moments for several exciplexes were obtained (Table 4).

The exciplex intermediates formed from styrylpyridines and amines enhance the isomerization for all the systems studied. However, quantitative analysis by spectrophotometrical measurements of the quantum yield of isomerization produced scattered data.

4. Discussion

There is little effect of the para-substituents on the absorption and emission maxima of the styrylpyridines, except for the methoxy substituent, which causes an observable bathochromic shift. The singlet excitation energies for all the substituted styrylpyridines calculated from the average values of the absorption and emission maxima are listed on Table 1. In general, the 2-StP samples had lower singlet excitation energies.

The fluorescence of all the styrylpyridines can be quenched by the tertiary amines. The quenching efficiency is proportional to the electron-donating ability of the donor (amines) and the electron-withdrawing ability of the acceptor (styrylpyridines), which indicates that electron transfer is involved in the quenching process.

The electron-accepting ability of the styrylpyridine can be visualized from the reduction potential measurements. The reduction potentials for substituted 3-StP are larger than those for 2-StP and 4-StP. The reduction potentials for 4-StP are smallest. There are linear correlations between the reduction potentials and Hammett σ_p constants (Fig. 3). The slopes and correlation coefficients are as follows: $\rho = 0.47$, $r = 0.99$ for 2-StP; $\rho = 0.41$, $r = 0.99$ for 3-StP; $\rho = 0.25$, $r = 0.99$ for 4-StP, except X≡CN. The reduction potentials for 4-StP are less sensitive to the substituents.

The Stern–Volmer quenching constants ($K_{sv} = k_q\tau$) are listed in Table 2 for the quenching of styrylpyridines by various amines. Singlet lifetimes were only available for 4′-Cl-3-StP (0.46 ns), 4′-H-3-StP (0.91 ns) and 4′-Me-3-StP (1.70 ns) [2], but the fluorescence quenching rate constants (k_q) calculated from these known lifetimes are listed also in Table 2. If the singlet lifetimes were unavailable, we used the average lifetime (1.0 ns) for the calculation. The values of k_q are near the rate of diffusion in *n*-hexane solution (3×10^{10} M^{-1} S^{-1}) [9]. The free energy change for the electron transfer can be calculated using

$$\Delta G^0 = E_d - E_a - E_{0,0} - 0.38 \quad (2)$$

The k_q values calculated are plotted with the free energy for electron transfer ΔG^0 in Fig. 4 for the 3-StP system. For ΔG^0 greater than -0.45 eV, the normal energy gap law according to Rehm and Weller is observed; however, there is a decreased quenching rate for the cyano substituent.

The observed energies E_1 at the exciplex fluorescence maxima can be compared with the calculated energies E_2 according to Rehm and Weller [10] as

$$E_2 = E_d - E_a - 0.15 \pm 0.1 \text{ eV} \quad (3)$$

where E_d and E_a represent the oxidation potential of the tertiary amines and the reduction potential of the styrylpyridines. There is a fair correlation between E_1 and E_2 (Fig. 5 and Table 3) in general, except for the 4′-cyano derivative. There is less correlation for TEA than for the other tertiary amines systems.

There is also a linear correlation between the exciplex maxima and the substituent constant σ_p for the substituted styrylpyridines. Electron-donating substituents shift the exciplex emission to shorter wavelengths and electron-accepting substituents shift the emission to longer wavelengths for all the tertiary amine–styrylpyridines. The

TABLE 3. Comparison of E_1 (observed energy at exciplex emission maximum) with E_2 (theoretical energy according to Rehm and Weller) and E_3 (dissociation enthalpy) of 4′-X-3-StP–tertiary amine and 4′-X-4-StP–tertiary amine exciplexes system in *n*-hexane

		CN	Cl	H	Isopropyl	Me	MeO
4′-X-3-StP							
DIPEA	λ (nm)	455	454.5	444.5	440	432	424.5
	E_1 (eV)	2.73	2.73	2.79	2.82	2.87	2.92
	E_2 (eV)	2.64	2.73	2.79	2.82	2.87	2.92
	E_3 (eV)	0.90	0.75	0.66	0.57	0.56	0.40
TBA	λ (nm)	463.5	461.5	451	447.5	441.5	442.5
	E_1 (eV)	2.68	2.69	2.75	2.77	2.81	2.80
	E_2 (eV)	2.68	2.76	2.87	2.90	2.92	2.94
	E_3 (eV)	0.79	0.64	0.55	0.46	0.45	0.29
TEA	λ (nm)	469.5	469	462	–	447	–
	E_1 (eV)	2.64	2.65	2.69	–	2.78	–
	E_2 (eV)	2.64	2.78	2.89	–	2.94	–
	E_3 (eV)	0.77	0.62	0.53	–	0.43	–
4′-X-4-StP							
DIPEA	λ (nm)	–	475.5	464.5	458	456.5	452
	E_1 (eV)	–	2.61	2.67	2.71	2.72	2.75
	E_2 (eV)	–	2.61	2.67	2.71	2.72	2.75
	E_3 (eV)	–	0.96	0.99	0.79	0.77	0.61
TBA	λ (nm)	–	483	476	471	471	464.5
	E_1 (eV)	–	2.57	2.61	2.63	2.63	2.67
	E_2 (eV)	–	2.61	2.66	2.70	2.71	2.73
	E_3 (eV)	–	0.85	0.88	0.88	0.66	0.50

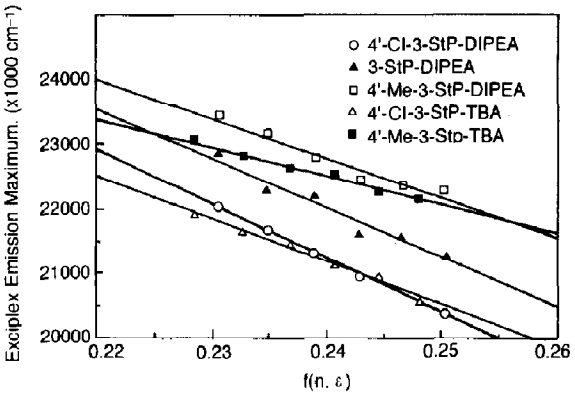

Fig. 2. Frequency of 4′-X-3-StP–amine exciplex fluorescence maxima *vs.* solvent polarizability: ○, 4′-Cl-3-StP—DIPEA; ◆, 3-StP–DIPEA; □, 4′-Me-3-StP–DIPEA; △, 4′-Cl-3-StP–TBA; ■, 4′-Me-3-StP–TBA.

TABLE 4. Dipole moment of 4′-X-3-StP–tertiary amine and 4′-X-4-StP–DIPEA exciplexes in *n*-hexane

		Cl	H	Me
4′-X-3-StP				
DIPEA	μ (debye)	17.5	16.6	14.9
TBA	μ (debye)	15.5	13.5	12.6
4′-X-4-StP				
DIPEA	μ (debye)		19.7	19.1

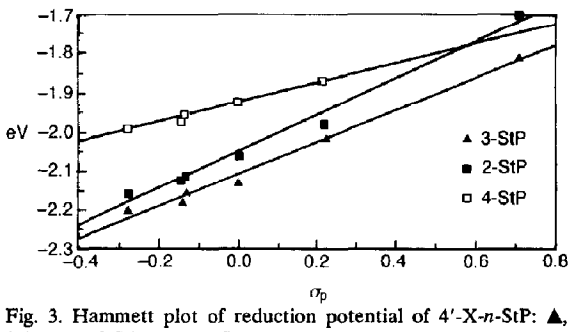

Fig. 3. Hammett plot of reduction potential of 4′-X-*n*-StP: ▲, 3-StP; ■, 2-StP; □, 4-StP.

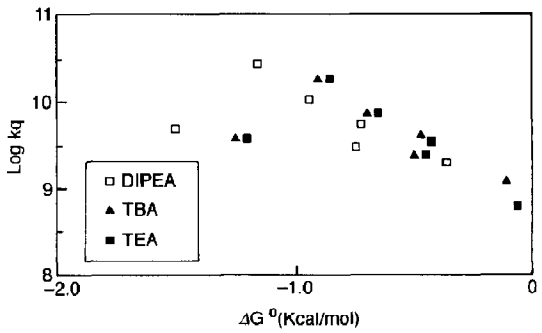

Fig. 4. Fluorescence quenching rate constant k_q of 4′-X-3-StP–amine as a function of free energy change in *n*-hexane: □, DIPEA; ▲, TBA; ■, TEA.

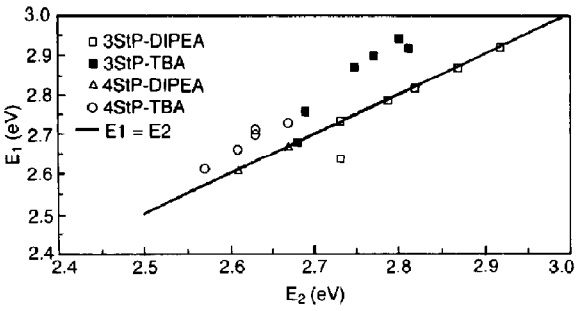

Fig. 5. Plot of experimental exciplex energy E_1 *vs.* theoretical energy E_2: □, 3-StP–DIPEA; ■, 3-StP–TBA; △, 4-StP–DIPEA; ○, 4-StP–TBA; —, $E_1 = E_2$.

slopes and correlation coefficients for the linear correlation between the exciplex maxima energies and Hammett σ_p constants are compared.

The slopes for the styrylpyridine–amine systems are negative, with fair to good correlation coefficients. The slopes of the DIPEA–StP systems are greater than those of the TBA–StP systems. The exciplex emission is more sensitive to the substituent effect when the donor is a stronger electron-donating amine. If we consider the same tertiary amine, the exciplex emission is most sensitive to the substituent effect for the 3-StP system. As for the linear Hammett correlation of the exciplex emission, the 4-StP system has shown a better correlation than the 3-StP system. This is consistent with our previous observation [5] that the thermodynamic stability of the exciplex formation is one of the contributing factors to the linearity of the Hammett correlation.

The enthalpy of dissociation for exciplex formation (E_3) can be calculated using [11].

$$E_3 = E_{0,0} - (E_d - E_a) - 0.13 \text{ eV} \quad (4)$$

It is found (Table 3) that the 4-StP–amine system shows larger E_3 values. The exciplex stability depends on the oxidation potential of the tertiary amines and the reduction potential of the substituted stilbenes. Hence, for certain stilbenes, DIPEA represents a better electron donor and gives more stable exciplexes [5]. For *n*-StP–amine systems, even though the reduction potentials for 2-StP are larger than those for 4-StP, the 2-StP–amine exciplexes are so unstable that it is barely observable. For *n*-StP systems, the 3-StP and 4-StP formed more stable exciplexes with DIPEA than with other amines. 4-StP and DIPEA formed the most stable exciplexes, even with a smaller reduction potential for 4-StP (compared with 3-StP). This may be because of the larger singlet energy for 4-StP.

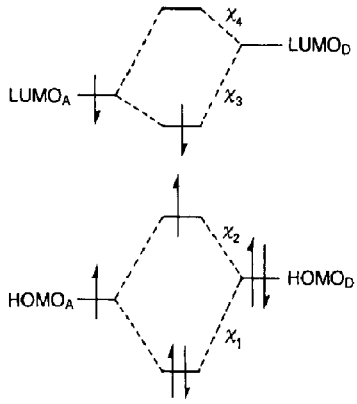

Fig. 6. FMO interaction for the formation of styrylpyridine–amine exciplexes.

The negative slopes for the styrylpyrdine–amine exciplex systems are similar to those of the stilbene–amine [5] and styrene–amine [12] exciplex systems, while the phenanthrene [6] exciplex systems show positive slopes. The frontier orbital theory [8] could be applied to explain the linear correlation. The new orbitals χ_1, χ_2, χ_3 and χ_4 for exciplex formation (Fig. 6) are derived from the HOMO$_D$–HOMO$_A$ (highest occupied molecular orbital) and LUMO$_D$–LUMO$_A$ (lowest unoccupied molecular orbital) interactions. The styrylpyridines served as acceptors while the tertiary amines were the donors. The main interaction is the LUMO$_D$–LUMO$_A$ interaction. An electron-donating substituent raises the LUMO$_A$ level, so the χ_3 level becomes higher in energy. The result is an increasing gap between χ_3 and χ_2, which corresponds to the exciplex emission energy.

The dipole moments obtained from the linear plot of the exciplex emission energy and solvent polarity of several exciplex systems are recorded in Table 4. The exciplex emission energies are very sensitive to changes in the solvent polarity, and the results give relatively high dipole moments for the exciplex systems (12–19 debye). The replacement of the nitrogen atom on the carbon atom site (styrylpyridine *vs.* stilbene) causes a large change in the dipole moments (4–10 debye for stilbene–amine exciplexes [5]).

5. Conclusions

Quenching rate constants increase as the free energy change of electron transfer becomes more exergonic, except for the cyano derivatives.

The correlation between the exciplex fluorescence maxima and the energies calculated ac-

cording to Rehm and Weller is better with better electron-donating amines. The exciplex fluorescent energies also give a linear Hammett correlation, except for the cyano derivatives.

The linear correlation can be explained with a simple frontier orbital diagram, while the exceptional cyano case can be ascribed to a change in the main interaction frontier orbitals — in this case from $LUMO_D$–$LUMO_A$ to $HOMO_D$–$HOMO_A$.

Acknowledgment

The financial support (NSC82-0208-M002-018) from National Science Council of ROC (Taiwan) is acknowledged.

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