

The Effect of Molecular Structure on the Photophysical Behavior of Substituted Styryl Pyrazine Derivatives

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Six styryl pyrazine compounds, some of which have steric hindrance to rotate and some have twist freedom, were synthesized in this work. The effects of solvent polarity and viscosity on the photophysical and luminescent behavior of these compounds were preliminarily studied. Results indicated that the blocking of the double-bond twist by a sufficiently rigid bridge increases fluorescence quantum yields dramatically and the rotation of a single bond connecting the double bond and the phenyl group is favorable to form a single-bond twisted state (T^*), which is the state responsible for the main channel of fluorescence emission. The reason for the higher fluorescence quantum yield of distyryl pyrazine was thought to be involved with the lower probability of transition from the Frank-Condon state (S_1) to the phantom state (P^*). Studies were also extended to develop a novel probe to detect the special microviscosity.

KEY WORDS: Styryl pyrazine derivatives; intramolecular charge transfer; multichannel excited state decay.

INTRODUCTION

The photophysical and photochemical properties of stilbene derivatives have been subjects of great interest for a long time.^(1,2) Recent studies indicated that stilbene derivatives with electronic donating-accepting substituents may show a very strong intramolecular charge transfer character, and therefore their luminescence increases significantly.^(3,4) Due to the fact that the decrease in photoisomerization was related to an increase in luminescence, a mechanism concerning excited-state decay with multichannels was proposed by Lapouyade *et al.* in 1993.^(5,6) In this argument, the double-bond twist is thought to be a main channel of nonradiation decays, while the single-bond twist is regarded as the favorable molecular conformation of radiation decay (luminescence decay). All these have been proved by theoretical

calculation and experimental measurements including the synthesis of some selectively conformational restricted bridging compounds. Based on these considerations, a three-state kinetic scheme was put forward to explain the results observed in photophysical measurements of these compounds.^(5,6)

Distyryl benzene (DSB) is a stilbene derivatives. In the early 1970s, DSB was found to be an efficient and stable laser dye.⁽⁷⁾ Compared to stilbene, DSB exhibits a higher fluorescence quantum yield, although no electronic push-pull substituent exists. The reason for this has not yet been thoroughly explained. Recently the photophysical behavior of distyryl pyrazine derivatives with a structure similar to that of DSB has been studied in our laboratory.⁽⁸⁾ After introducing different electronic push-pull groups, as stilbene derivatives, it was found that the intramolecular charge transfer influences the luminescent behavior of these compounds. In this work, the photophysical behaviors of these compounds with an intramolecular steric hindered structure were investigated under various conditions. The results indicate that

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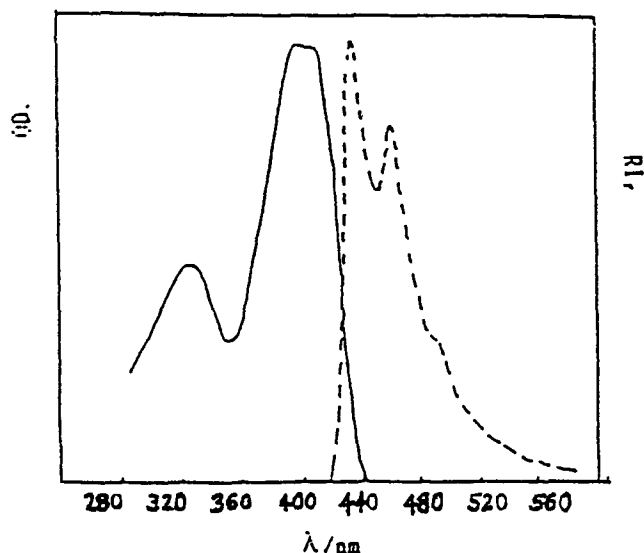


Fig. 1. Absorption and fluorescence spectra of compound IV in cyclohexane at room temperature. The vertical axis is arbitrary units.

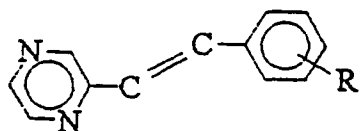
the three-state kinetic scheme can also be used to explain the photophysical behaviors of the derivatives studied. The experimental results also provided some valuable information on the practical use of these compounds.

EXPERIMENTAL

Materials

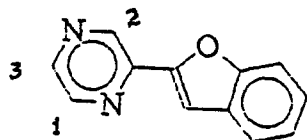
The compounds studied in this work are as follows:

- (1) styryl pyrazine (I),
- (2) 2-hydroxystyryl pyrazine (II),



Compound 1

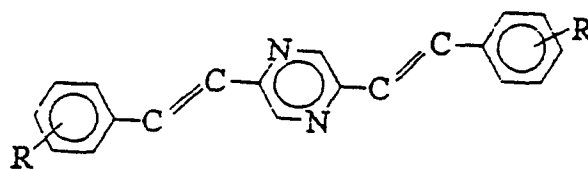
- (3) benzofuran-2-pyrazine (III),



Compound 2

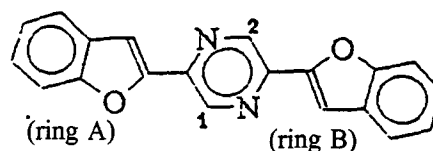
- (4) distyryl pyrazine (IV),

- (5) 2,2'-Dihydroxydistyryl pyrazine (V), and



Compound 3

- (6) dibenzofuran-2,2'-pyrazine (VI).



Compound 4

All compounds were prepared by ourselves. Compounds I, II, IV, and V were synthesized from corresponding aldehydes and methyl pyrazine, compounds III and VI were obtained by dehydration and cyclization from corresponding 2-hydroxystyryl pyrazine derivatives in the presence of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as a dehydrating agent in dry ethanol. The products obtained were purified by thin-layer chromatography and recrystallization and characterized by IR, MS, and ¹H-NMR. Solvents used in this work were purified by the methods described by Perrin et al.⁽⁹⁾ except for acetonitrile (spectroscopically pure) and glycerol (AR).

Measurements

Absorption and emission spectra were recorded on a Hitachi 330 UV-vis spectrophotometer and a Hitachi MPF-4 fluorescence spectrophotometer, respectively. The fluorescence quantum yields were determined using a solution of fluorescein in 0.1 M sodium hydroxide as a standard (quantum yield taken as 0.93).⁽¹⁰⁾ The different environmental temperatures below 0°C were obtained by changing the ratio of liquid nitrogen to ethanol.

RESULTS AND DISCUSSION

The absorption and emission spectra of compound IV in cyclohexane are shown in Fig. 1; those of other compounds are similar to that of IV. The wavelengths of absorption and emission maxima are given in Tables I and II.

The results in Table I show that the absorption maximum of monostyryl pyrazine II is shifted to a

Table I. Wavelength of Absorption Maxima (nm) of the Studied Compounds (10^{-5} M) in Different Solvents at Room Temperature

Solvent	ET(30)	$\lambda_{\text{abs max}}$					
		I	II	III	IV	V	VI
Cyclohexane	31.2	317	325	377	382	—	394
Ether	34.6	317	325	378	379	390	390
THF	37.4	317	325	382	382	399	394
Ethylacetate	38.1	317	325	380	385	394	391
Acetonitrile	46.0	317	330	378	380	393	390

Table II. Wavelength of Fluorescence Maxima^a (nm) of the Studied Compounds (2×10^{-6} M) in Different Solvents at Room Temperature

Solvent	Debye constant, $\epsilon - 1/\epsilon + 2$	$\lambda_{\text{abs max}}$					
		I	II	III	IV	V	VI
Cyclohexane	0.25	376	390	421	419	—	412
Ether	0.53	317	401	423	421	441	417
Ethylacetate	0.63	382	409	426	423	446	425
THF	0.69	386	412	428	426	450	391
Acetonitrile	0.92	390	425	429	430	459	432

^aFluorescence maxima were obtained by 320-nm (I), 325-nm (II), 380-nm (III and IV), and 390-nm (V and VI) excitation, respectively.

longer wavelength than that of compound I, indicating that the introduction of a hydroxy group influenced the absorption spectra to some degree. On the other hand, the wavelength of the absorption maximum of compound III is much longer than those of compounds I and II. This suggests that the bridging structure may change the molecular conformation dramatically, leading to a molecular coplanar structure and, consequently, causing a greater effect on the conjugation of the tested compound. Comparing the peak wavelength in the absorption spectrum of distyryl pyrazine with that for monostyryl pyrazine, it is easy to see that for monostyryl pyrazine derivatives II and III, an evident difference exists in their absorption spectra, but the absorption maxima of distyryl pyrazine derivatives V and VI are close to each other. This indicates that the bridging of distyryl pyrazine derivatives has only a small effect on the molecular conformation compared with that of the unbridged one. This result also shows that the introduction of a second styryl group to the pyrazine ring has an effect similar to that of the bridging of the monostyryl pyrazine on their absorption spectra (see Table I, in which the absorption maxima of compounds III and IV are at almost the same wavelengths). Based on these considerations, it may be concluded that the molecular

conformation of distyryl pyrazines is located, more or less, in a partial coplanar condition, whether or not they are bridged. This conclusion was also proved by the ¹H-NMR spectral data. For compound III, the chemical shifts of the protons (H1, H2, and H3) located in the pyrazyl ring were 8.54, 9.18, and 8.67 ppm. But for compound VI, the δ value of H1 became smaller (8.09 ppm), and the δ value of H2 showed almost no change (8.10 ppm). These results imply that the proton (H1) which experienced an upfield shift was affected by shielding from the noncoplanar moiety of the molecule, i.e., the proton is located in the shielding field of the benzofuran ring (ring A), and proton H2 is located in the deshielding field of another benzofuran ring (ring B). The above results indicate that the pyrazyl ring is coplanar with ring B and at a dihedral angle with ring A.

The results compiled in Table II show that compounds II and V, in which a hydroxy group was introduced, exhibit very clear features of intramolecular charge transfer. Their emission peak wavelengths shift to red with increasing solvent polarity; for example, for compound II, the peak wavelength shifted from 390 nm (cyclohexane) to 425 nm (acetonitrile), and for compound V, from 441 nm (ether) to 459 nm (acetonitrile). The range of wavelength variation was about 20–30 nm. However, for compounds III, IV, and VI, the lower degree of intramolecular charge transfer results in less variation of the fluorescence maxima in different solvents, such as the peak wavelength of compound III shifting from 423 nm (ether) to 429 nm (acetonitrile); that of compound IV, from 421 nm (ether) to 430 nm (acetonitrile); and that of compound VI, from 417 nm (ether) to 432 nm (acetonitrile). The range of wavelength variation of these compounds in different solvents is only from 10 to 15 nm. These results imply that the longer emission wavelengths or the larger Stokes shifts of compounds II and V are attributable to their stronger intramolecular charge transfer.

The solvent-induced shifts of the emission and absorption spectra (Stokes shift) can be linearly correlated with the solvent polarity parameter Bilot-Kawaski (BK) values:⁽¹¹⁾

$$\nu_a - \nu_f = \frac{2(\mu_e - \mu_g)^2}{cha^3} \text{BK} + \text{cons.}$$

where ν_a and ν_f are the wavenumbers of the absorption and emission peaks in the same solvent, respectively; $\nu_a - \nu_f$ is the Stoke's shift value; μ_e and μ_g are the dipole moments in the excited and ground states, respectively; a is the Onsager cavity radius of the molecule, which is generally 0.7 times the molecular length or calculated

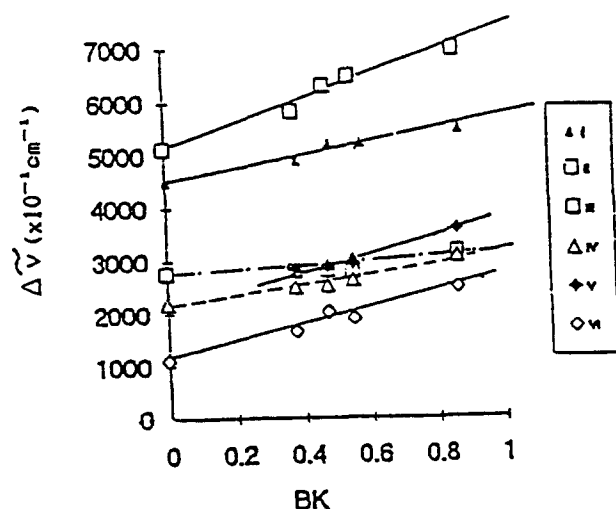


Fig. 2. Solvatochromic plot of the studied compounds: the Stoke's shift $\nu_s - \nu_r$ versus the solvent polarity parameter BK.

Table III. The Change in Dipole Moment Between the Excited and the Ground States ($\Delta\mu_{eg}$) of the Studied Compounds

	I	II	III	IV	V	VI
$\Delta\mu_{eg}$ (D)	1.04	1.72	0.84	1.27	2.66	1.84

Table IV. Fluorescence Quantum Yields^a of the Studied Compounds in Different Solvents

Solvent	Φ_f					
	I	II	III	IV	V	VI
Cyclohexane	0.0047	0.0037	0.45	0.43	—	0.98
Ether	0.0051	0.0086	0.49	0.44	0.71	1.01
THF	0.0056	0.0093	0.49	0.49	0.61	0.94
Ethyl acetate	0.0057	0.011	0.47	0.47	0.58	0.90
Acetonitrile	0.0025	0.017	0.41	0.46	0.45	0.90

^aValues were obtained by 320-nm (I), 325-nm (II), 380-nm (III and IV), and 390-nm (V and VI) excitation, respectively.

from the molecular weight and specific gravity;⁽¹²⁾ BK is one of the parameters describing the solvent polarity; and c and h are the velocity of light and the Planck constant, respectively. The BK value is correlated with the static dielectric constant (ϵ) and the refractive index (n) of solvents, as follows:

$$BK = \left(\frac{\epsilon - 1}{2\epsilon + 2} - \frac{n^2 - 1}{2n^2 + 1} \right) / \left[\left(1 - \frac{n^2 - 1}{2n^2 + 1} \right)^2 \left(1 - \frac{\epsilon - 1}{2\epsilon + 1} \right) \right]$$

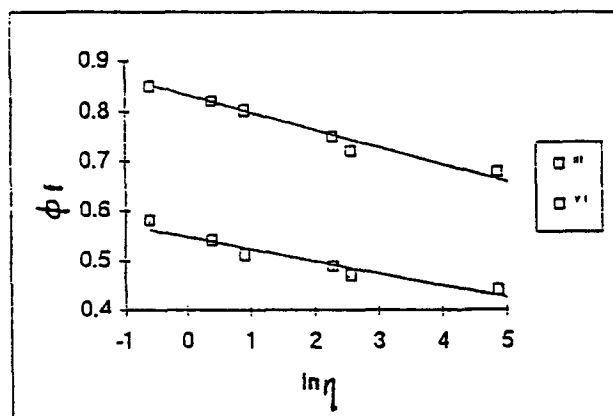


Fig. 3. Plot of fluorescence quantum yield versus viscosity (cp) in methanol + glycerol for compounds III and VI.

The Stoke's shifts of the studied compounds in different solvents are plotted against the BK values in Fig. 2. The changes in the dipole moment between the excited and the ground states are obtained from the slopes of the straight lines in Fig. 2 and are summarized in Table III. Although the approximation of the a value used may affect the precision of the results, some valuable information can still be obtained. It is shown in Table III that the difference in the dipole moment of compounds II and V between the excited and the ground states is greater than that of other compounds. It is further confirmed that a stronger charge transfer exists within these two compounds.

The fluorescence quantum yields of these compounds in different solvents are listed in Table IV. From Table IV, the following results can clearly be obtained.

(1) All distyryl pyrazine derivatives have higher fluorescence quantum yields than monostyryl substituted derivatives do, which is consistent with results obtained previously.⁽⁶⁾

(2) The bridged compounds (III, VI) exhibit higher fluorescence quantum yields than the nonbridged compounds (II, V) do. This indicates that blocking of the double bond is able to prevent photoisomerization and increase the fluorescence quantum yields.

(3) The fluorescence quantum yields of compounds II and V, which have a stronger charge transfer ability than the compounds without a hydroxide group do, depend on the solvent polarity. The fluorescence quantum yield of compound V clearly decreases with a solvent polarity increase, showing an obvious positive solvatochromic effect.⁽¹³⁾ On the contrary, for compound II, the fluorescence quantum yield increases with solvent polarity, exhibiting a negative solvatochromic effect. As is

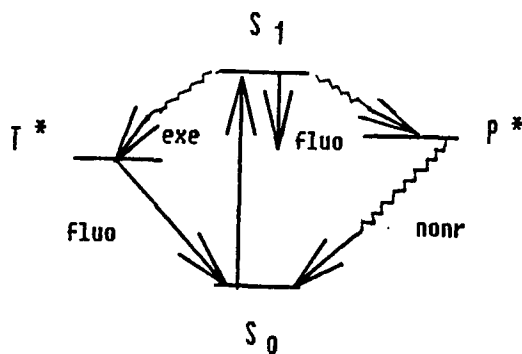
Table V. Fluorescence Quantum Yields^a of Compounds in Different Alcoholic Solvents

	Methanol	Ethanol	<i>i</i> -Propanol	<i>n</i> -Butanol	Ethylene glycol	Glycerol
Dielectric constant	31.2	25.7	18.6	16.1	38.7	41.4
Viscosity (cp)	0.59	1.22	2.4	2.91	17.4	945
Φ_f						
III	0.66	0.65	0.63	0.59	0.54	0.40
VI	0.90	0.89	0.87	0.81	0.75	0.60

^a Φ_f values were obtained by 380-nm (III) and 390-nm (VI) excitation; respectively.

well-known, the negative solvatokinetic effect is caused by different factors such as the biradicaloid charge transfer,⁽¹⁴⁾ the proximity effect,⁽¹⁴⁾ and others.⁽¹⁵⁾ It is very clear that for compound II, all factors described above existed due to the presence of a nitrogen atom in the pyrazine ring and a free double bond. But it is noteworthy that a negative solvatokinetic effect is observed for compound II, while a positive solvatokinetic effect is observed for compound V. A possible reason is that compound V may have a behavior like that of compound III in which the double bond was blocked, meaning that the biradical formation should be reduced, which would suppress the negative solvatokinetic effect. On the other hand, the larger change in the dipole moment between the excited and the ground state for compound V compared with the other compounds means that a strong intramolecular charge transfer existed during the photoinduced process. This may be the main reason for the positive solvatokinetic effect that occurred for compound V. Based on the suggestion proposed by Lapouyade *et al.*,⁽⁶⁾ a similar three-energy level scheme, depicted as follows, was used to explain the photophysical properties of the studied compounds in different solvents.

Regarding Scheme I, it was suggested that, besides the local excited state (S_1) formed by the Frank-Condon transition and the phantom state (P^*) formed by the dou-



Scheme I.

ble-bond twist, another twist state (T^* probably exists due to the single-bond twist. According to the emission spectra, the double bond of distyryl pyrazine derivatives IV and V was free, but the P^* -state formation of these compounds was very limited. A possible explanation is that, in this case, a T^* state exists and its energy level is near to, or lower than, that of the P^* state; it is probable that a great deal of transition from the S_1 state to the T^* state occurs and promotes molecular emission dramatically. However, the compounds with a free double bond, such as compound II, were excited; the excited molecule could be easy to relax from the S_1 state to the P^* state, and the energy absorbed would be lost by strong nonradiation decay from the P^* state.

As discussed above, the geometries of compounds III and VI in the S_1 state are different from those in the T^* state, and their fluorescence quantum yields change very little with the polarity of the environment, so it is reasonable to imagine that they are influenced by the surrounding microviscosity.

The fluorescence quantum yields of the studied compounds in solvents of different viscosity, mixed at different ratios of methanol and glycerol, are exhibited in Fig. 3. This shows that the fluorescence quantum yields of compounds III and VI, with rigidized structures, decrease with increasing solvent viscosity. The explanation could be that, for compounds III and VI and, especially, for compound III, with a coplanar structure, because the radiation decay from the T^* state is the main relaxation for the emission of these molecules, the increasing viscosity makes the internal rotation of the pyrazine ring difficult, thus decreasing the Φ_f value. These results were obtained in media with an almost-constant polarity. The effect of environmental viscosity on Φ_f values in media of different polarities was also investigated in this work, as shown in Table V.

From Table V, it is difficult to find any regularity of the fluorescence quantum yields of compounds III and VI according to the static dielectric constants of different alcoholic solvents. If the Φ_f value were correlated

with the solvent viscosity, it could be found that Φ_f decreases with increasing viscosity. The results clearly show that, for these two blocked compounds, the surrounding viscosity has a prominent effect on the magnitude of the Φ_f values, indicating that there is conformation relaxation of the excited molecule for compound **III** and **VI**. Furthermore, due to the lower bathochromic effect in different polar solvents for the two rigidized compounds, they are able to be used as novel fluorescence probes for detecting the environmental viscosity.

CONCLUSION

A series of compounds with a rigidized or freely rotated structure was synthesized in this work and their photophysical behavior was preliminarily studied. The conclusions were drawn that blocking of the double bond for both monostyryl pyrazine and distyryl pyrazine is the important pathway for increasing the fluorescence quantum yields. It is suggested that the excited molecule of distyryl pyrazine is favorable for relaxing from the S_1 to the T^* state and its energy level is the same as, or even lower than, that of the P^* state, which makes it difficult to relax from the S_1 to the P^* state, resulting in higher fluorescence quantum yields for distyryl pyrazine than for monostyryl pyrazine. Because of the lesser bathochromic effect in different polar solvents for the two

rigidized compounds **III** and **VI**, they could be developed as novel fluorescence probes for detecting the environmental viscosity.

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