Photoisomerization of (*E*)-1-(2-Naphthyl)-2-pyrazin-2-ylethylene

Sang Chul Shim * and **Mi Suk Kim**
Department of Chemistry Korea Advanced Institute of Science and Technology PO Box 150, Cheongryang, Seoul, 130-650, Korea

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The fluorescence quantum yield of (*E*)-1-(2-naphthyl)-2-pyrazin-2-ylethylene (2-NPyE) is very low compared with 2-styrylnaphthalene (2-StN) due to very rapid radiationless decay processes and is sensitive to solvent polarity. The $E \longrightarrow Z$ photoisomerization proceeds through both the singlet and triplet manifolds with relatively low quantum yields at room temperature. The singlet mechanism is favoured in polar solvents due to the decrease in intersystem-crossing efficiency with increasing solvent polarity.

Aza-analogues of stilbene have received much attention because the states (n,π^*) introduced by nitrogen atoms significantly affect the photochemical and photophysical properties.[1-3] The vibronic interation of the (n,π^*) state with the lowest (π,π^*) state increases radiationless transitions (internal conversion and intersystem crossing) to deactivate the excited molecules, particularly in the *ortho* and *para* aza-derivatives.[4,5] Styrylpyridines (StPs) and 1,2-dipyridylethylenes (DPEs) have been studied by Mazzucato[1] and Whitten.[6] These compounds show very low fluorescence and photoisomerization quantum yields compared with stilbene and a singlet mechanism has been proposed for the direct photoisomerization. A fast internal conversion is the major deactivation path of pyridine and could also be an important process in 2- and 4-StPs and 2,2′- and 4,4′-DPEs. Therefore, most of the molecules in the excited singlet states are deactivated by internal conversion at room temperature but intersystem crossing becomes effective in a rigid matrix at low temperature compared with the isomerization path. The *meta* isomers, 3-StP and 3,3′-DPE, behave differently since they have near nodes in the *meta* position in both π and π^* orbitals. This precludes intercombinational transition between the (n,π^*) state and the lowest (π,π^*) state. The direct $E \longrightarrow Z$ photoisomerization of styrylpyrazine[7] and bispyrazinylethylene (BPyE)[8] in which $\Phi_{isc} = 1.0$ and $\Phi_{ph} = 1.0$, proceeds through the triplet manifold, consistent with the laser flash-photolysis results indicating efficient intersystem crossing in contrast with stilbene and other aza-analogues.

Replacement of one or both phenyl groups of stilbene with aromatic polycyclic group (naphthyl and phenanthryl *etc.*) may have two major effects. The strong steric interaction between the aryl group and the ethylenic hydrogens and the lowest excited state of an aromatic nature noticeably affect the rate of photoisomerization of the *E* compound. The consequences of the naphthyl substitution in 2-styrylnaphthalene (2-StN) are high fluorescence and relatively low photoisomerization quantum yields at room temperature, probably because of an activated internal rotation in S_1 state.[9] The steric interaction can be important in determining the mixtures of conformers originating from rotation of the aryl group about a quasi-single bond between the aryl group and the ethylenic carbon atom.[10]

1-(2-Naphthyl)-2-pyrazin-2-ylethylene (2-NPyE), in which the phenyl ring in styrylnaphthalene[11] is replaced by a pyrazine ring, would have both the (π,π^*) and (n,π^*) states due to the nitrogen atoms. In this study, spectroscopic properties and $E \longrightarrow Z$ photoisomerization of 2-NPyE are investigated under various conditions to determine the effect of (n,π^*) state and the large condensed naphthalene ring on the excited state behaviour.

Experimental

Materials.—1-(2-Naphthyl)-2-pyrazin-2-ylethylene (2-NPyE) was prepared by a Wittig reaction of the ylide obtained from 2-bromomethylnaphthalene (a mixture of geometrical isomers in a ratio of 50:50 was obtained). The *E* and *Z* compounds were separated and purified by low pressure liquid chromatography ($MeOH-H_2O$ 2.5:1, v/v) and the purity checked with h.p.l.c. and/or g.c.

(*E*)-2-NPyE: yield *ca.* 30%; m.p. 136–137 °C; *m*/*z* 232 (molecular ion); $\nu_{max.}$(KBr pellet) 985 cm^{-1} (=C–H out-of-plane bending vibration of the *E* double bond); $\delta_H(CDCl_3)$ 8.5 (3 H, m, pyrazine ring) and 7.5 (9 H, m, naphthalene ring and ethylenic).

(*Z*)-2-NPyE: yield *ca.* 30%: m.p. 52–53 °C; $\nu_{max.}$(KBr pellet) 735 cm^{-1} (=C–H out-of-plane bending vibration of *Z*-alkene); $\delta_H(CDCl_3)$ 8.3 (3 H, m, pyrazine ring), 7.5 (7 H, m, naphthalene ring), 7.1 (1 H, d, ethylenic, *J* 12 Hz), and 6.6 (1 H, d, ethylenic, *J* 12 Hz).

Butane-2,3-dione (Aldrich) was purified by vacuum distillation. Azulene (Aldrich) was purified by vacuum sublimation. Commerically available 2-bromomethylnaphthalene and pyrazinecarboxylic acid (Aldrich), and triphenyl phosphine (Fluka) were used without further purification.

Spectroscopic Measurements.—U.v. absorption spectra were recorded on a Cary-17 spectrophotometer. Fluorescence spectra were measured on an Aminco–Bowman spectrophotofluorimeter with an Aminco XY recorder at room temperature and at 77 K with modification of the cell compartment. The recorded emission spectra were corrected for the response characteristics of the photomultiplier tube (1P21, S-4 spectral response) and the instrument monochromator as a function of wavelength.

Quantum-yield Measurements.—The fluorescence quantum yields at room temperature were determined relative to quinine hydrogensulphate [Φ_f (298 K) = 0.546 in H_2SO_4 0.1 mol dm^{-3}]. The absorbance was kept as low as possible, usually below 0.1, in order to minimize errors due to front surface imprisonment and inner-filter effects.

The $E \longrightarrow Z$ photoisomerization quantum yields were determined under conditions in which all the incident light was absorbed ($A > 2.0$, 1×10^{-3} mol dm^{-3} solution). The solutions in sealed Pyrex ampoules were irradiated with a Hanovia 450 W medium-pressure mercury arc lamp (Type 679A-36) in a merry-go-round apparatus. Mercury emission lines of 366.0 and 435.8 nm were isolated by the following filters: 366.0 nm, Corning glass filters CS 0–52 and 7–37; 435.8 nm, $NaNO_2$ (7.5 g) in aqueous solution (100 cm^3) and $CuSO_4 \cdot 5H_2O$ (0.44 g) in

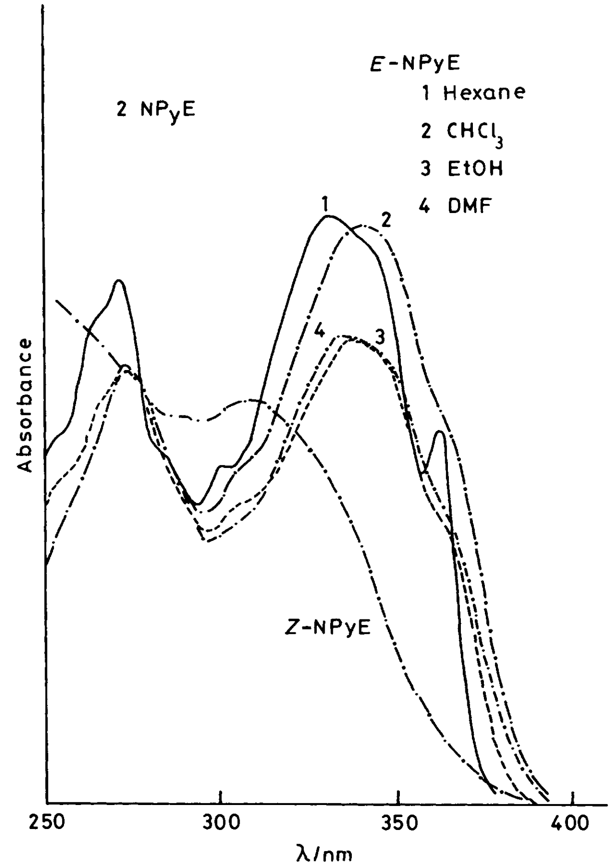

Figure 1. U.v. absorption spectra of 2-NPyE.

Table 1. Fluorescence maxima and quantum yields of 2-NPyE, 2-StN, and its aza-derivatives.

Compound	Solvent	λ_{max}	Φ_f	Compound	Φ_f[a]
2-NPyE	Hexane	367	0.06	2-StN[b]	*A*; 0.83 *B*; 0.50
	Et_2O	394	0.09	2,2′-NPE[b]	0.045
	CH_2Cl_2	410	0.24	2,3′-NPE[b]	*A*; 0.25 *B*; 0.85
	$CHCl_3$	414	0.23	2,4′-NPE[b]	0.25
	EtOH	443	0.41	StQx[c]	0.002
	MeOH	452	0.41		

[a] In Hexane. [b] From ref. 9. [c] From ref. 14.

aqueous NH_4OH (2.7 mol dm^{-3}; 100 cm^3). Ferrioxalate actinometry was used to monitor the intensity of the exciting light.[12] Quantitative analyses were carried out by g.c. on a Varian Vista 6000 gas chromatograph. Quantum yields of photoisomerization were determined by using low conversions (1–5%) to prevent the back-reaction.

Molecular-mechanics Calculation.—Molecular-mechanics calculations were performed by using MACROMODEL with MM-2 force-field and the BDNR method as a minimum algorithm. In searching for energy minima, a series of geometries corresponding to small, systematic internal rotation around both the two essential single bonds connecting the naphthyl group and pyrazinyl group were input and allowed to relax fully by using the BDNR minimization scheme. If a particular conformation was found initially to occupy a local energy minimum, conformations with dihedral angles slightly different from those in that first-discovered minimum energy geometry were input, and minimization was repeated again to ensure the accurate identification of an equilibrium geometry.

Results and Discussion

Spectral Properties.—The absorption spectra of two isomers of 2-NPyE are shown in Figure 1. The absorption band of the *E* isomer at 328 nm is probably due to the (π,π*) transition of the conjugated ethylenic system and is red-shifted with respect to that of 2-StN (315 nm)[13] due to the increase in conjugation as a consequence of reduced steric crowding originating from the presence of nitrogen atoms in place of CH groups. The (π,π*) nature of the absorption band is confirmed by the red shift in polar solvents.

Table 1 shows the fluorescence maxima and quantum yields (Φ_f) of 2-NPyE in various solvents. As the solvent polarity increases, the fluorescence maximum is shifted to long wavelength indicating that the lowest and fluorescent excited state is the $^1(\pi,\pi^*)$ state. The fluorescence quantum yields are lower than those of 2-StN and affected by the solvent polarity due to the presence of (*n*,π*) state. In azastilbenes, the vibronic coupling of the (*n*,π*) state with the lowest (π,π*) state increases non-radiative transitions to deactivate the excited molecules. The proximity effect reduces the fluorescence quantum yield of 2-NPyE compared with the corresponding hydrocarbon, 2-StN. However, the decrease of Φ_f due to proximity effects is very low compared with 2-styrylquinoxaline (StQx). A large proximity effect in StQx due to the closeness of the lowest singlet excited (π,π*) and (*n*,π*) states leads to a drastic decrease in Φ_f.[14] The lowest (*n*,π*) and (π,π*) states in NPyE are mixed slightly and show a small proximity effect. This observation is supported by salt effect on fluorescence of 2-NPyE. Alkali-metal cations are expected to raise the energy of $^1(n,\pi^*)$ state in a manner similar to polar solvents. However, the fluorescence efficiency of 2-NPyE is not affected by LiCl, NaOAc, and KOAc salts, suggesting that the $^1(n,\pi^*)$ level is not close enough to $^1(\pi,\pi^*)$ even though the energy level of $^1(n,\pi^*)$ is raised by polar solvents (EtOH:H_2O 1:1, v/v), and the fluorescent $^1(\pi,\pi^*)$ state is slightly mixed with $^1(n,\pi^*)$ state.

Conformational Equilibria.—The absorption maxima are slightly red-shifted with increasing the solvent polarity, but blue-shifted in highly polar solvents, as shown in Figure 1, probably due to the existence of conformers originating from rotation of the aryl groups (naphthyl, pyrazinyl) about quasi-single bonds between the aryl groups and the ethylenic carbon atoms.[10] MM-2 force field and a BDNR calculation suggested that the postulated pyrazinyl conformers (A, B) are different from each other in energy and planarity and are separated by a barrier of about 4.4 kcal mol^{-1},* as shown in Figure 2. The calculated energy difference between the pyrazinyl conformers is estimated to be 2.4 kcal mol^{-1}, and hence conformer A is predominant at room temperature. The naphthyl conformers (*a*, *b*) are similar in energy and are separated by a barrier of about 4.0 kcal mol^{-1}. The relative mole fraction of the naphthyl conformers at equilibrium are predicted to be the same, *i.e.*, 0.5. However, this may not be the same in solution because of the solvation. The composition of the two conformers, *a* and *b*, changes on varying the solvents and one conformer, being predominant in polar solvents, absorbs shorter-wavelength u.v. light and λ_{max} are blue shifted in highly polar solvents.

The fluorescence spectra of 2-NPyE at various excitation wavelengths display structured shape with two components, probably the sum of the spectra of each conformer in equilbrium

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* 1 cal = 4.1868 J.

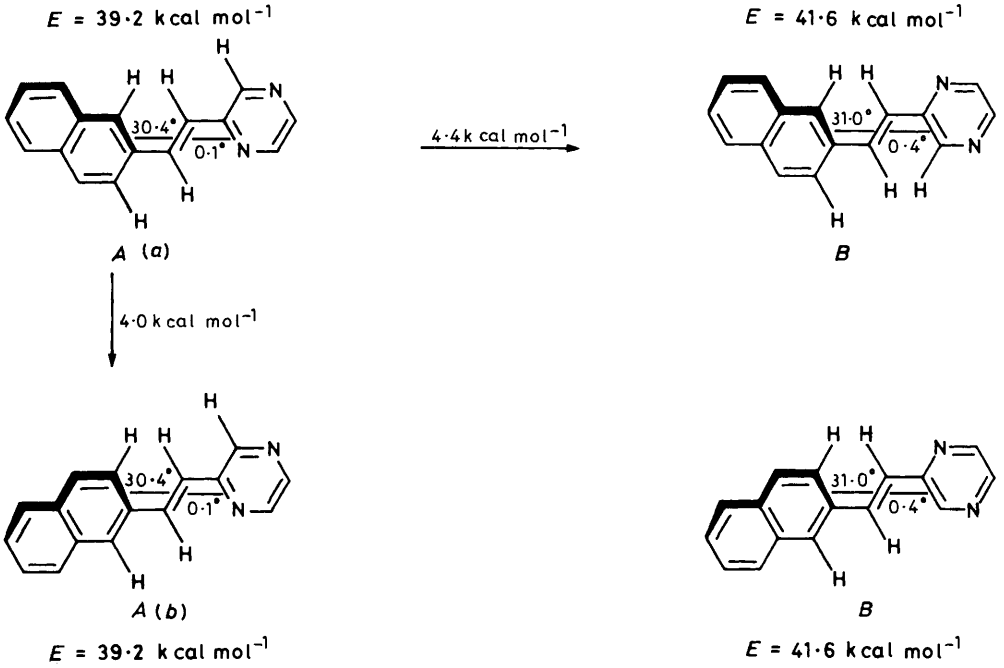

Figure 2. Geometries and energies of 2-NPyE conformers by MM-2 and BDNR calculations.

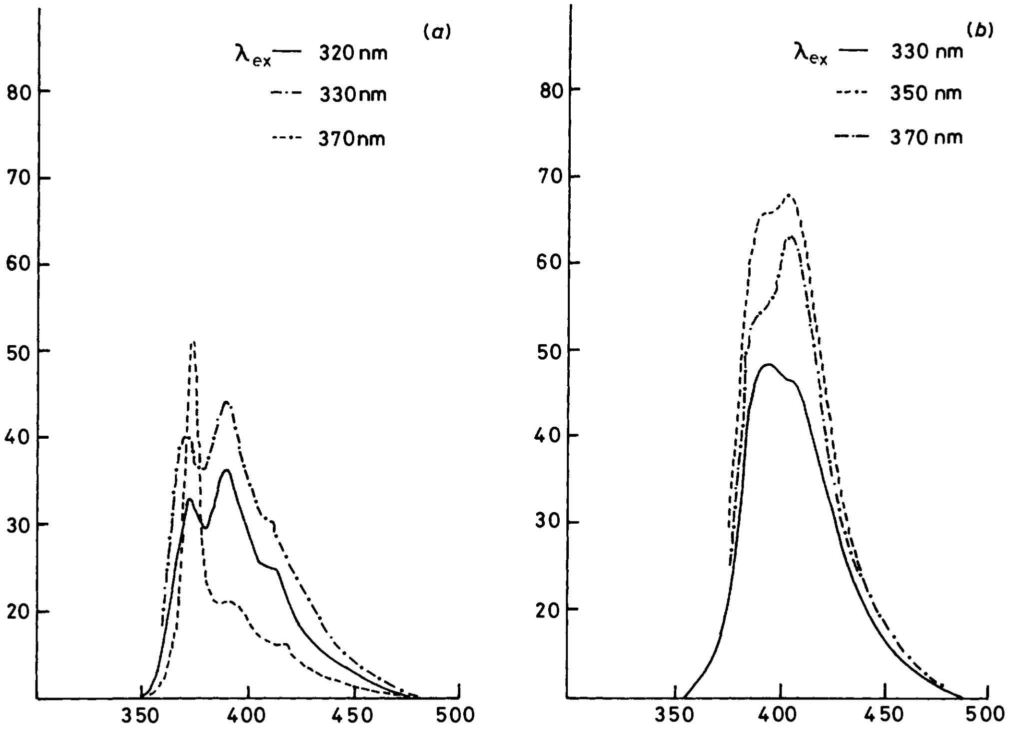

Figure 3. Fluorescence spectra of 2-NPyE (*a*) in hexane at room temperature (*b*) in ethanol at 77 K.

Table 2. Quantum yield of direct photoisomerization of 2-NPyE, 2-StN, and its aza-derivatives in hexane.

Compound	Φ_c	Compound	Φ_c
2-NPyE	0.24	2-StN[a]	0.16
2-StP[b]	0.22	2,2′-NPE[a]	0.27
3-StP[b]	0.52	2,3′-NPE[a]	0.15
4-StP[b]	0.37	2,4′-NPE[a]	0.26

[a] From ref. 10. [b] From ref. 1.

(Figure 3). On changing the excitation wavelength, the composition of the excited conformers changes because of the different absorption characteristics of each conformer and the contribution of each conformer to the fluorescence spectra is different, thus changing the shape of the fluorescence spectra.

E ⟶ Z *Photoisomerization.*—The direct photoisomerization quantum yields of 2-NPyE (Table 2) are relatively low and give values between those of StPs and 2-StN. The result is attributed to an activated internal rotation in the S_1 state. The internal rotation is slower than that of StPs but faster than that

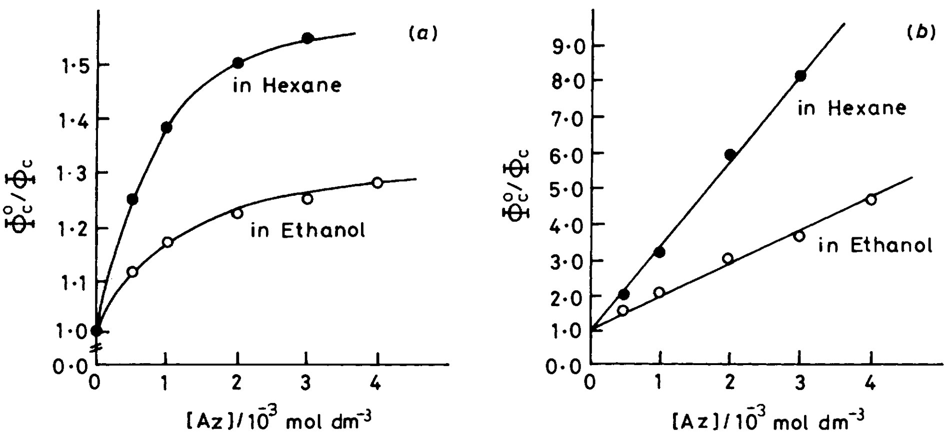

Figure 4. Stern–Volmer plots for the $E \longrightarrow Z$ photoisomerization quantum yield of 2-NPyE (*a*) *via* singlet and triplet excited states (*b*) *via* a triplet excited state.

Table 3. Azulene effect on direct photoisomerization of azastilbene derivatives.

Compound		Φ_c		
		$\Phi_c(S)$	$\Phi_c(T)$	$k_q\tau$
2-NPyE	Hexane	0.14 (60%)	0.10 (40%)	2 700
	EtOH	0.06 (70%)	0.02 (30%)	1 200
4-StP[a]		0.37		18
4,4′-DPE[a]		0.003		70
BPE[b]			0.35	1 100

[a] From ref. 6. [b] From ref. 8.

Table 4. Sensitized[a] photoisomerization quantum yields and calculated intersystem-crossing and internal-conversion quantum yields of 2-NPyE.

Solvent	Φ_c^{sens}	Φ_{isc}	Φ_{ic}	Φ_f
Hexane	0.30	0.33	0.33	0.06
Ethanol	0.33	0.06	0.35	0.47

[a] Biacetyl-sensitized photoisomerization at 435.8 nm.

of 2-StNs because of the steric interaction between the aryl groups and the ethylenic hydrogens. The quantum yields are higher than that for 2-StN probably due to the presence of a (n,π^*) state which can lead to rapid radiationless processes such as internal conversion or intersystem crossing followed by isomerization.

Assuming that azulene quenches only one state, the singlet or the triplet state, the Stern–Volmer plot should be linear.

$$\Phi_c^\circ/\Phi_c = 1 + k_q\tau[\mathrm{Az}] \qquad (1)$$

However the Stern–Volmer plots for 2-NPyE shown in Figure 4(*a*) are curved suggesting that the $E \longrightarrow Z$ photoisomerization of 2-NPyE occurs through both the singlet and triplet excited states.[15] The following photoisomerization mechanism is proposed in which the product is formed from two excited states of 2-NPyE, and both states may be affected by the quencher.

$$\mathrm{t} \xrightarrow{h\nu} {}^1\mathrm{t} \qquad (2)$$

$$^1\mathrm{t} \xrightarrow{k_f} \mathrm{t} + h\nu \qquad (3)$$

$$^1\mathrm{t} \xrightarrow{k_{ic}} \mathrm{t} \qquad (4)$$

$$^1\mathrm{t} \xrightarrow{k_{isc}} {}^3\mathrm{t} \qquad (5)$$

$$^1\mathrm{t} \xrightarrow{k_p} {}^1\mathrm{p} \qquad (6)$$

$$^1\mathrm{p} \xrightarrow{k_d} \alpha\mathrm{t} + (1 - \alpha)\mathrm{c} \qquad (7)$$

$$^1\mathrm{p} + \mathrm{Az} \xrightarrow{k_q} \mathrm{t} + \mathrm{Az} \qquad (8)$$

$$^3\mathrm{t} \xrightarrow{k_p'} {}^3\mathrm{p} \qquad (9)$$

$$^3\mathrm{p} \xrightarrow{k_d'} \beta\mathrm{t} + (1 + \beta)\mathrm{c} \qquad (10)$$

$$^3\mathrm{p} + \mathrm{Az} \xrightarrow{k_q'} \mathrm{t} + \mathrm{Az} \qquad (11)$$

Here t, c, and p represent *E*, *Z*, and twisted geometry of 2-NPyE, while k_f, k_{ic}, k_p, k_d, and k_{isc} are the rate constants for fluorescence, internal conversion, twisting, decay, and intersystem crossing, respectively. Subtraction of $\Phi_c(S)$, the quantum yield from the singlet excited state, from the total quantum yield at any azulene concentration provides $\Phi_c(T)$, the quantum yield from the triplet excited state. A Stern–Volmer plot for $\Phi_c(T)$, as expressed in equation (12), should be linear

$$\frac{\Phi_c^\circ(T)}{\Phi_c(T)} = \frac{\Phi^\circ - \Phi_c^\circ(S)}{\Phi - \Phi_c(S)} = 1 + k_q\tau_T[\mathrm{Az}] \qquad (12)$$

with a slope equal to $k_q\tau_T$. The value of $[\Phi^\circ - \Phi_c(S)]/[\Phi_c - \Phi_c(S)]$ *vs.* [Az] is shown in Figure 4(*b*). The calculated values are reported in Table 3 together with values for some azastilbene derivatives.

The quantum yield of intersystem crossing was calculated by using the following equation (13)

$$\Phi_{isc} = \frac{\Phi_{c(T)}^{\mathrm{dir\ at\ 366\ nm}}}{\Phi_c^{\mathrm{sen\ at\ 435.8\ nm}}} \qquad (13)$$

and tabulated in Table 4 together with internal conversion quantum yield, Φ_{ic}, which can be approximated by the following equation

$$\Phi_{ic} = 1 - \Phi_f - \Phi_{t\rightarrow p} - \Phi_{isc} \qquad (14)$$

where $\Phi_{t\rightarrow p}$ is practically twice the experimental photoisomerization quantum yield because of the partitioning factor $\alpha = 0.5$. The solvent polarity affects the intersystem crossing quantum yields strongly. The calculated Φ_{isc} in hexane is large and the

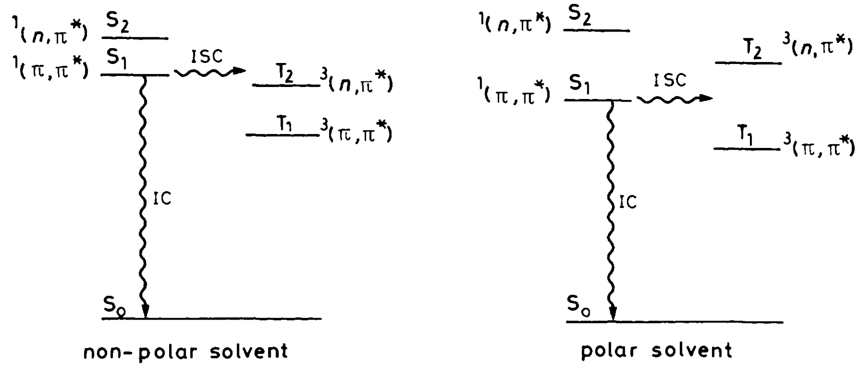

Figure 5. Plausible energy levels of 2-NPyE.

large values for organic molecules not possessing heavy atoms are found for systems undergoing $(\pi,\pi^*) \longrightarrow (n,\pi^*)$ transitions with small energy gaps.[17,18] The energy of the (n,π^*) state becomes higher as the polarity of the solvent increases; the $^3(n,\pi^*)$ state becomes higher than the $^1(\pi,\pi^*)$ state in polar solvents. As the polarity of the solvent increases, the process of intersystem crossing changes from $^1(\pi,\pi^*) \longrightarrow {}^3(n,\pi^*)$ to $^1(\pi,\pi^*) \longrightarrow {}^3(\pi,\pi^*)$ as shown in Figure 5. Based on theoretical considerations, El-Sayed[4] concluded that intersystem crossing between different orbital states should proceed much more rapidly than transitions between states of the same type. Therefore, the intersystem-crossing quantum yields decrease as the polarity of the solvent increases. This prediction is experimentally verified with external heavy-atom effects on Φ_{isc}.[19] The external heavy-atom effects on intersystem crossing tend to be minimal for $(\pi,\pi^*) \longrightarrow (n,\pi^*)$ transitions because the process already possesses substantial spin–orbit interactions. Assuming that the only process competing with fluorescence is intersystem crossing (*i.e.*, The calculated Φ_{ic} are little affected by solvent polarity) one can conclude that observed quenching of fluorescence is due to an increased rate of intersystem crossing in the presence of the heavy atom. In practice the fluorescence of 2-NPyE in hexane is not quenched by ethyl iodide while a heavy-atom effect on Φ_f in ethanol was observed, $k_q\tau = 6.3$. This result supports the intersystem-crossing processes presented in Figure 5.

Conclusions

The presence of the nitrogen atom has a noticeable influence on the photochemical and photophysical behaviour of 2-NPyE. The introduction of the (n,π^*) states reduces the fluorescence quantum yield compared with the corresponding hydrocarbon, 2-StN and increases non-radiative decay paths. The $E \longrightarrow Z$ photoisomerization of 2-NPyE proceeds through two excited states, the triplet and singlet states, and the singlet state is favoured in polar solvents. As the solvent polarity increases, Φ_{isc} decreases because the intersystem-crossing process changes from $^1(\pi,\pi^*) \longrightarrow {}^3(n,\pi^*)$ to $^1(\pi,\pi^*) \longrightarrow {}^3(\pi,\pi^*)$ due to the inversion of the relative energy levels of the $^1(\pi,\pi^*)$ and $^3(n,\pi^*)$ state and the decrease of k_{isc} leads to the enhancement of the fluorescence quantum yield. The consequence of the naphthyl substitution is a relatively low photoisomerization quantum yield and the existence of conformers originating from rotation of the naphthyl group.

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