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Molecular Structure and Photochemistry of (*E*)- and (*Z*)-2-(2-(2-Pyridyl)ethenyl)indole. A Case of Hydrogen Bond Dependent One-Way Photoisomerization

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Abstract: The molecular structure, electronic spectra, and photoisomerization of (*E*)- and (*Z*)-2-(2-(2-pyridyl)ethenyl)indole have been investigated. The *E* isomer exists in the ground state as a mixture of two rotational isomers, whereas the *Z* isomer exists predominantly as a single conformer due to the presence of an intramolecular hydrogen bond. The structure and energy of the configurational and conformational isomers have been investigated by means of NMR spectroscopy and molecular mechanics. In the case of the *E* isomer, the less polar conformer is favored in nonpolar solvents and the more polar conformer in polar solvents. The more polar conformer has a low barrier for singlet state isomerization and thus has a short singlet lifetime and high isomerization quantum yield. The less polar conformer has a longer singlet lifetime and lower quantum yield for photoisomerization. The *N*-methyl derivative of the *E* isomer exists as a single rotamer with photochemical behavior similar to that of the long-lived rotamer. The hydrogen-bonded conformer of the *Z* isomer does not undergo photoisomerization due to either the occurrence of rapid nonradiative decay or a hydrogen bond dependent barrier for twisting. As a consequence, irradiation of the *E* isomer results in one-way *E* → Z photoisomerization in both polar and nonpolar solvents. A minor conformer of the *Z* isomer may be responsible for the observation of weak fluorescence and inefficient photoisomerization in polar solvents. The *N*-methyl derivative of the *Z* isomer undergoes photoisomerization.

Introduction

The 2-(2-(2-pyridyl)ethenyl)indoles (*Z*-**1** vs *E*-**1**) are members of a class of molecules in which photoisomerization results in the formation or disruption of an intramolecular hydrogen bond (Chart 1).[1-6] The intramolecular hydrogen bond can influence the ground state equilibrium between configurational and conformational isomers as well as photophysical and photochemical behavior. The occurrence of one-way *E* → Z photoisomerization of 2-(2-(2-pyridyl)ethenyl)indole (**1**) was first reported by Snieckus and co-workers[1] in 1973. The selective formation of *Z*-**1** vs *E*-**1** in the Wittig reaction and the lower energy ultraviolet absorption maximum for *Z*-**1** were attributed to the presence of an intramolecular hydrogen bond in the *Z* isomer. The synthesis of the *N*-methyl derivatives (**2**) was also reported; however, their photoisomerization was not investigated. The 3-(pyridyl)propenamides (**3**) undergo one-way isomerization in nonpolar solvents but two-way isomerization in polar solvents which disrupt the intramolecular hydrogen bond in *Z*-**3**.[3] Methyl urocanate (**4**)[4] undergoes two-way isomerization in both nonpolar and polar solvents. Both the 5-(2-pyridylmethylidene)-3-pyrrolin-2-ones (**5**)[5] and the 1-(2-pyrrolyl)-2-(2-quinolyl)ethene (**6**)[6] form photostationary states highly enriched in the *Z* isomer. Competing adiabatic hydrogen transfer to form the tautomers **5′** and **6′** may be responsible for inefficient photoisomerization of the *Z* isomers.[5b,6]

Our interest in the effects of intramolecular hydrogen bonding on the photoisomerization of arylethylenes[2-6] prompted reinvestigation of the spectroscopy and photochemistry of **1**. As is the case for many other 1,2-diarylethylenes,[7] *E*-**1** and *Z*-**1** exist as mixtures of rotational isomers (conformers) which are in equilibrium in the ground state but do not equilibrate in the excited singlet state. The two fluorescent conformers of *E*-**1** differ in polarity and thus their ground state equilibrium is strongly solvent dependent. The excited singlet states of these conformers display similar fluorescence rate constants but substantially different lifetimes and isomerization rate constants, the shorter-lived conformer undergoing more rapid isomerization. The *N*-methyl derivative *E*-**2** exists as a single conformer and provides a model for the long-lived conformer of *E*-**1**. *Z*-**1** exists predominantly as a single hydrogen bonded conformer in both polar and nonpolar solvents. The lowest excited singlet state of the major conformer of *Z*-**1** does not undergo isomerization at room temperature. The intramolecular N–H··N stretch may be involved in a rapid nonradiative decay process.

Results

Molecular Structure. The synthesis and spectroscopic characterization of *E*-**1** and *Z*-**1** and their *N*-methyl derivatives *E*-**2** and *Z*-**2** were reported by Snieckus and co-workers.[1] The configurational isomers *E*-**1** and *Z*-**1** are readily distinguished by ^{1}H NMR spectroscopy on the basis of the downfield shift of the N–H proton in *Z*-**1** vs *E*-**1** (δ = 13.95 vs 8.35 ppm in $CDCl_3$) and by IR spectroscopy on the basis of the lower

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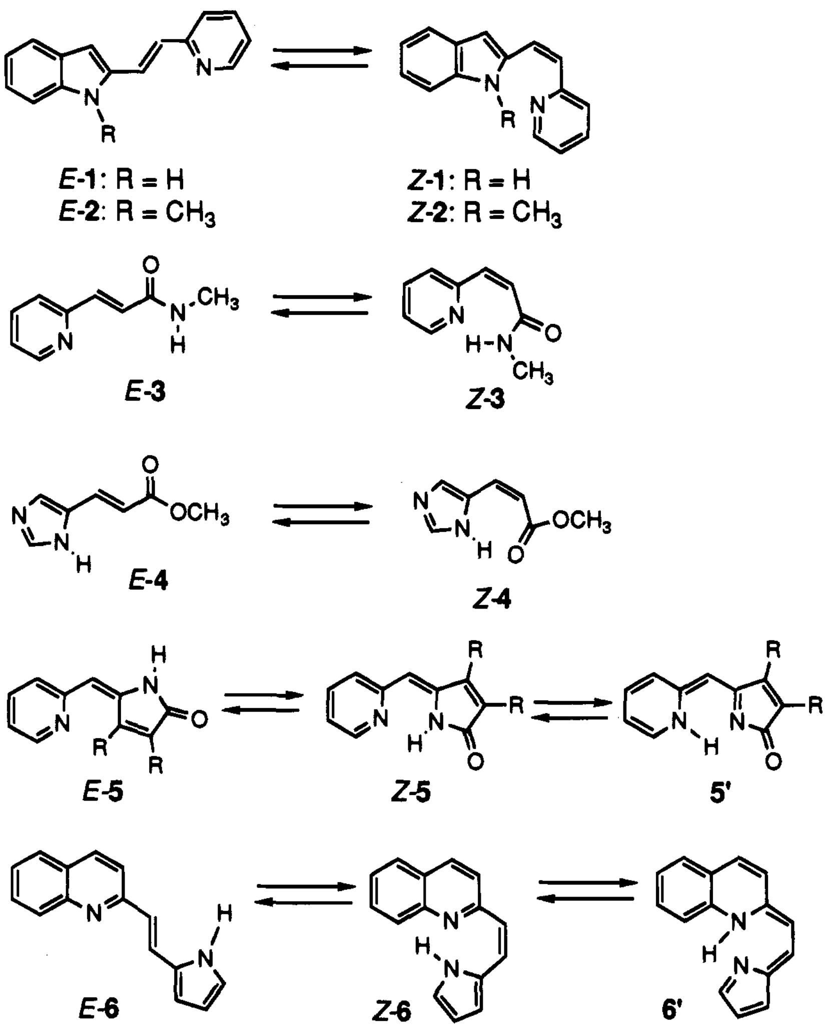
Chart 1



frequency of the N–H stretch at high dilution in *Z*-**1** vs *E*-**1** (ν = 3000 vs 3400 cm^{-1} in $CHCl_3$).

Both *E*-**1** and *Z*-**1** can exist as a mixture of four conformers as a consequence of rotation about the indole–vinyl and pyridyl–vinyl bonds (Chart 2). We have employed solvent-dependent NOE studies to establish that the intramolecular hydrogen bond in *Z*-**3** is present in $CDCl_3$ but not in DMSO solution.[3] In the case of *Z*-**1**, irradiation of N–H in either $CDCl_3$ or DMSO solution results in large NOEs for both indole H_7 (7.2% and 8.8%, respectively) and pyridine H_6 (6.9% and 9.5%, respectively). NOEs for the vinyl protons are too small to measure, indicating that *Z*-**1** exists predominantly as the hydrogen-bonded conformer *Z*-**1a** in both solvents. The chemical shifts of the vinyl protons of *E*-**1** change systematically with increasing solvent polarity (C_6D_6, $CDCl_3$, DMSO-d_6), indicative of a change in conformer populations. However, NOE studies failed to provide definitive evidence for the identity of the major conformer(s) in these solvents. On the basis of analogy with previous studies of the conformers of 2-styrylpyrrole[8a] and 2-styrylpyridine,[8b] the vinylindole conformers *E*-**1a** and *E*-**1b** are anticipated to be of comparable energy and more stable than their vinylpyridine conformers *E*-**1c** and *E*-**1d**. Similarly, *Z*-**1a** and *Z*-**1b** are anticipated to be more stable than their vinylindole conformers *Z*-**1c** and *Z*-**1d**. The results of simple gas phase MAXIMIN2[9] calculations are consistent with this expectation.

Free-radical-initiated isomerization of (*Z*)-stilbene and other 1,2-diarylethylenes has been effected using irradiation of iodine[10a] and diphenyl diselenide[10b] as the radical source. Whereas iodine reacts rapidly with *E*-**1** and *Z*-**1** to form brown precipitates upon irradiation, solutions of diphenyl diselenide and *E*-**1** and *Z*-**1** are stable in the dark and undergo clean photoinitiated isomerization. Irradiation (420 nm) in benzene solution (6×10^{-3} M in both reactants) results in the formation of a 1.4:1 *Z*/*E* ratio, whereas irradiation in diethyl ether results in a 0.42:1 *Z*/*E* ratio. The analogous reactions of *E*-**2** or *Z*-**2** result in the formation of a 0.02:1 *Z*/*E* ratio in benzene solution. The free energy difference between *E*-**1** and *Z*-**1** in the solid state was investigated using differential scanning calorimetry (DSC).[2] The DSC thermograms at a rising rate of temperature of 2.5–7 °C min^{-1} showed that *Z*-**1** is more stable than *E*-**1** in the solid state by 6.9 kcal/mol.

Absorption Spectra. The electronic absorption spectra of *E*-**1** and *Z*-**1** in methylcyclohexane solution are shown in Figure 1. The absorption maximum of *Z*-**1** is at longer wavelength than that of *E*-**1**, which displays a larger extinction coefficient and some vibrational structure. Increasing solvent polarity results in a small red-shift and loss of structure for *E*-**1** and a small blue-shift for *Z*-**1** (Table 1). Absorption spectral data for *E*-**2** and *Z*-**2** are also reported in Table 1. The absorption maxima of *E*-**2** are at longer wavelength than those for *E*-**1**,

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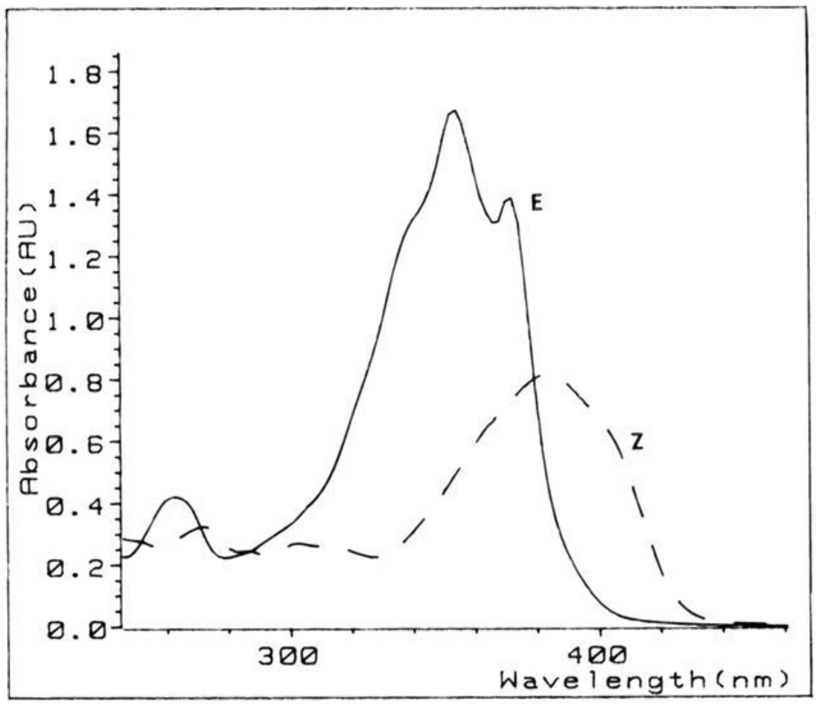
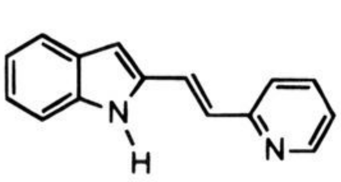
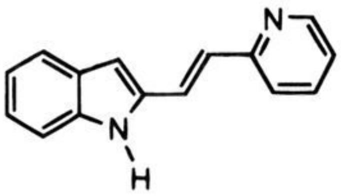


Figure 1. Electronic absorption spectra of 5×10^{-5} M *E*-**1** (—) and *Z*-**1** (- - -) in methylcyclohexane soltuion.

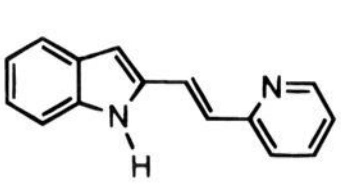
Chart 2



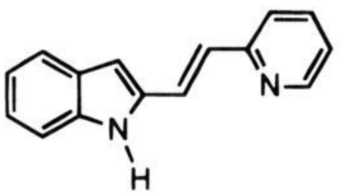
E-**1c**



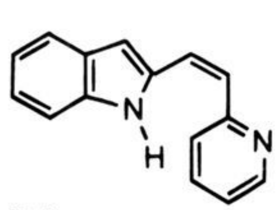
E-**1d**



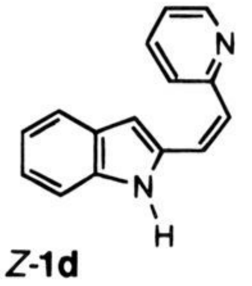
E-**1a**



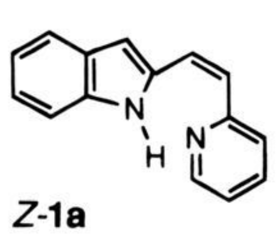
E-**1b**



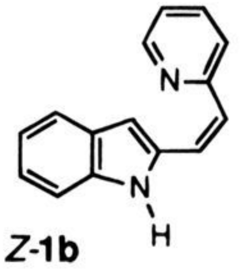
Z-**1c**



Z-**1d**



Z-**1a**



Z-**1b**

whereas the maxima for *Z*-**2** are at significantly shorter wavelength than those for *Z*-**1**.

The electronic structure and spectra of the four conformers of *E*-**1** and the hydrogen-bonded conformer *Z*-**1a** have been investigated by means of semiempirical INDO/S-SCF-CI (ZINDO) calculations using the algorithm developed by Zerner and co-workers.[11] Molecular structures were those calculated using MAXIMIN2.[9] The ZINDO-derived highest occupied and lowest unoccupied molecular orbitals of *E*-**1a**, *E*-**1b**, and *Z*-**1a** are shown in Figure 2. The appearance of the orbitals *E*-**1c** and *E*-**1d** is similar to those of *E*-**1a** and *E*-**1b**, respectively. In each case the HOMO and LUMO are π-bonding and antibonding with respect to the ethylene. The energy of the HOMO is well separated energetically from that of the two lower energy π-bonding orbitals and the pyridyl nitrogen nonbonding orbital. The location of the nonbonding orbitals below the highest energy filled π-orbitals is consistent with ordering of ionization energies in the photoelectron spectrum of 2-vinylpyridine.[12] In the case of *Z*-**1a** the nonbonding orbital (n_1 in Figure 2) displays interaction between the pyridyl and indole nitrogens, which is absent in the nonbonding orbitals of *E*-**1**.

Table 1. Electronic Absorption Data

isomer	solvent	λ_{max}, nm	ϵ (λ_{max})
E-**1**	methylcyclohexane	354, 372	33 500, 27 800
	benzene	350	35 900
	diethyl ether	352	34 000
	ethanol	358	31 200
Z-**1**	methylcyclohexane	384	16 400
	benzene	379	25 300
	diethyl ether	374	18 800
	ethanol	372	18 600
E-**2**	benzene	362	19 700
	ethanol	364	19 600
Z-**2**	benzene	338	10.900
	ethanol	332	10 900

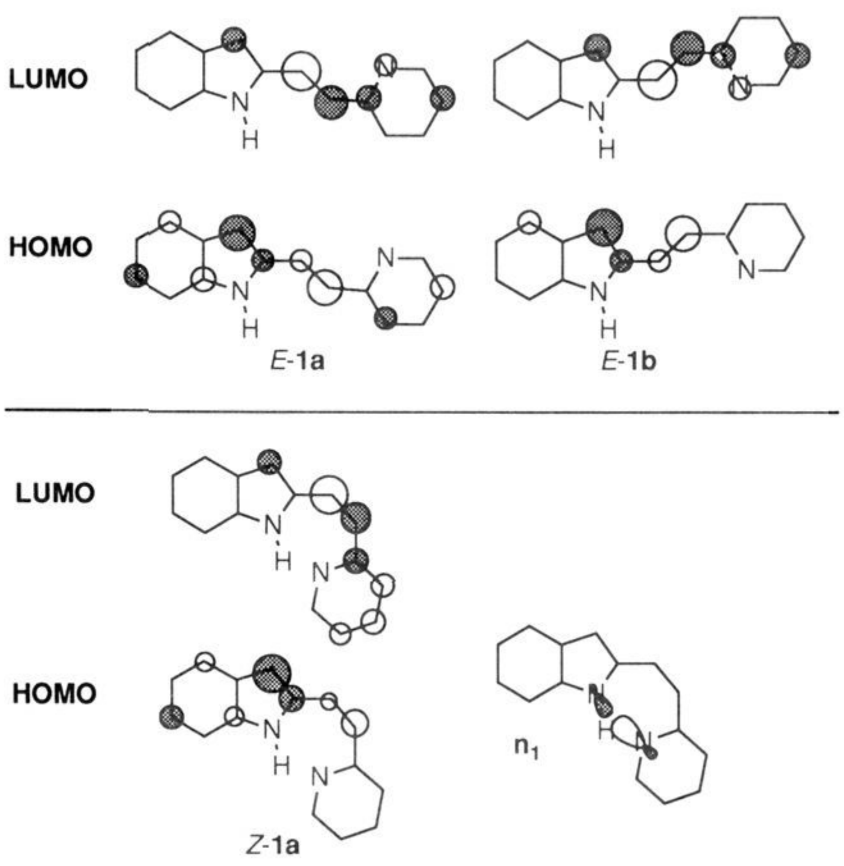


Figure 2. Frontier molecular orbitals of *E*-**1a**, *E*-**1b**, and *Z*-**1a**.

The lowest energy transition for all four conformers of *E*-**1** and of *Z*-**1a** is a relatively pure, allowed HOMO → LUMO, π → π* transition. Forbidden n → π* transitions lie at slightly higher energies than the lowest energy π → π* transition in all cases. Higher energy π → π* transitions with extensive configuration interaction and low oscillator strengths can account for the weak higher energy absorption bands (Figure 1). The calculated energies and oscillator strengths for the π → π* transition and ground state dipole moments of *E*-**1a**, *E*-**1b**, and *Z*-**1a** are reported in Table 2. The longer wavelength and lower oscillator strength calculated for *Z*-**1a** vs *E*-**1a** or *E*-**1b** are in agreement with the observed spectra (Figure 1).

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Table 2. Calculated Absorption Spectral Data and Dipole Moments

isomer	λ_{max}, nm	f	η, D
E-**1a**	339	1.32	4.30
E-**1b**	347	1.12	2.36
Z-**1a**	359	0.74	4.96

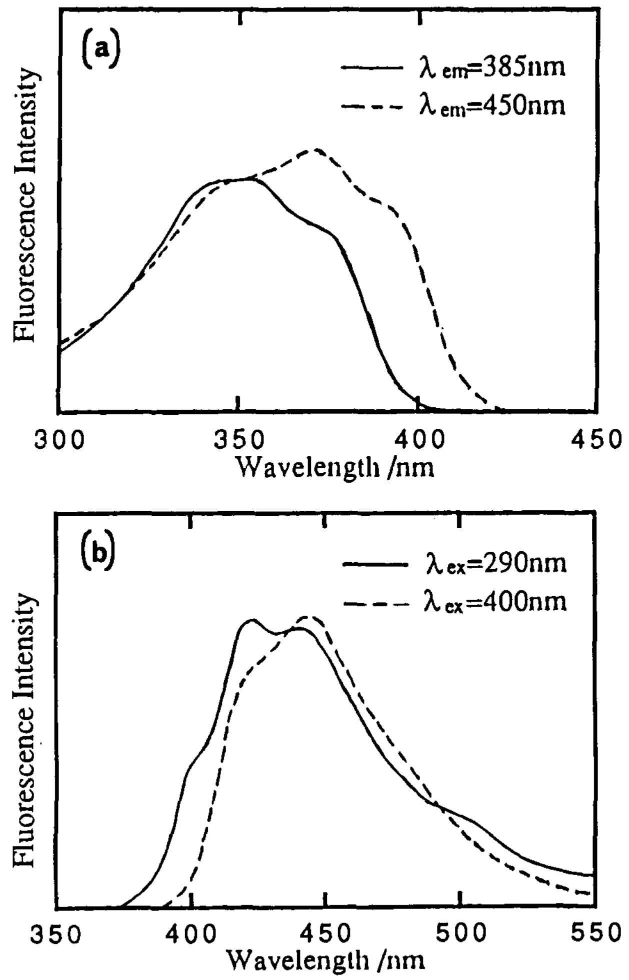

Figure 3. Fluorescence excitation (a) and emission (b) spectra of *E*-**1** in benzene solution at room temperature.

Fluorescence. The room temperature fluorescence emission and excitation spectra of *E*-**1** in benzene solution are shown in Figure 3. Excitation in the long wavelength edge of the absorption spectrum (400 nm) results in emission which is red-shifted with respect to that obtained using 290 nm excitation. Complementary changes in the fluorescence excitation spectrum are observed when different emission wavelengths are used. Fluorescence quantum yields and lifetimes for *E*-**1** in several solvents are reported in Table 3. The room temperature fluorescence emission of *E*-**1** in more polar solvents is structureless and displays only small shifts in emission maximum with changes in excitation wavelength. The fluorescence emission and excitation spectra of *E*-**1** at 77 K in an EPA glass formed by rapid cooling are shown in Figure 4. The spectra display well-defined, excitation or emission wavelength-dependent, vibrational structure. Excitation at 390 nm results in emission which is red-shifted with respect to that obtained using 350 nm excitation. Smaller changes are observed in the excitation spectra obtained when the emission is monitored at 390 vs 420 nm.

Table 3. Fluorescence Spectral Data for *E*-**1** and *E*-**2**

isomer	solvent	$\lambda_{ex}{}^{a}$	Φ_f	$\lambda_{ex}{}^{b}$	τ_s, ns^{c} (%)	τ_L, ns^{c} (%)
E-**1**	benzene	300	0.36	362	0.12 (11)^{d}	2.3 (89)^{d}
		400	0.47	390		2.3 (>95)
	methylcyclohexane			350	0.6 (13)	2.3 (87)
	dichloromethane			350	0.4 (10)	2.3 (90)
	diethyl ether	354	0.16	350	0.4 (31)	2.7 (69)
	acetonitrile			350	0.4 (42)	2.7 (58)
	ethanol, EPA	354	0.07^{e}	350	0.3 (82)^{f}	2.4 (18)^{f}
	DMSO			350	0.4 (78)	2.8 (22)
E-**2**	benzene	360	0.66	350		3.0^{g}
	ethanol	360	0.48	350		3.1^{g}

[a] Excitation wavelength for fluorescence quantum yield measurement. [b] Excitation wavelength for fluoresecence decay measurement. [c] Short-lived and long-lived components of fluorescence decay as determined at the fluorescence maximum and their percent contribution to total fluorescence. [d] Data obtained using a pulsed laser and streak scope. τ_s = 0.3 ns and τ_L = 2.6 ns determined by single photon counting. [e] Data for ethanol solution. [f] Data for EPA solution. [g] Single exponential decay.

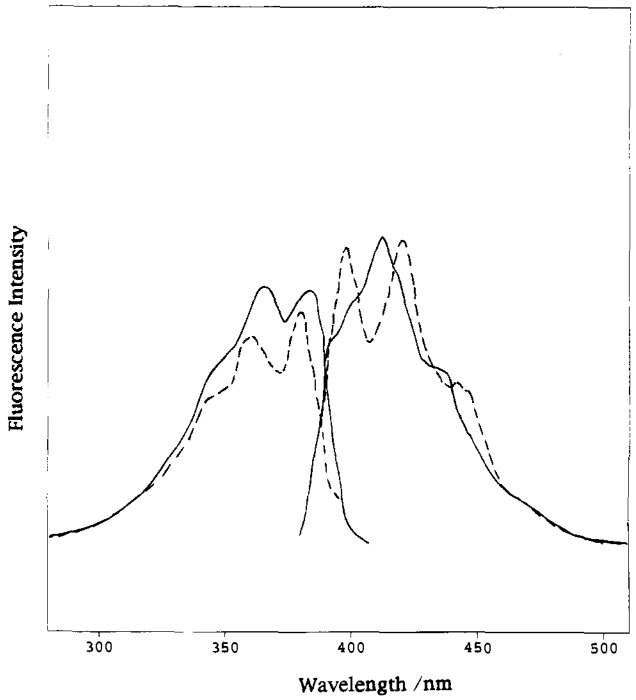

Figure 4. Fluorescence emission [λ_{ex} = 350 (—) or 390 nm (- - -)] and excitation [λ_{em} = 420 (—) or 408 nm (- - -)] spectra of *E*-**1** in an EPA glass at 77 K.

Fluorescence quantum yield (Φ_f, estimated accuracy ±10%) and lifetime data obtained in several solvents at room temperature are reported in Table 3. The value of Φ_f in benzene solution is larger for excitation at 400 vs 300 nm. Distinctly smaller values of Φ_f are obtained using 354 nm excitation in diethyl ether, ethanol, and dichloromethane solution ($\Phi_f = 0.12$ in the latter solvent). Dual exponential fluorescence decay is observed when the excitation wavelength is near the absorption maximum in several solvents (350 or 362 nm), while single exponential decay is observed in benzene solution for excitation at 390 nm. The lifetimes of the longer-lived fluorescence (τ_L) are 2.3–2.8 ns in the solvents investigated. The lifetimes of the shorter-lived fluorescence (τ_s), as determined by means of time-correlated single photon counting using a gated arc lamp (ca. 2 ns fwhm), are 0.3–0.6 ns, near the time resolution of this instrumentation. Fluorescence decays in benzene solution were also measured using a pulsed laser (2 ps fwhm) and streakscope. The value of τ_s obtained with this apparatus is shorter than that obtained by single photon counting (0.12 vs 0.3 ns) and is considered more reliable. The actual values of τ_s for the other solvents in Table 3 may also be slightly shorter

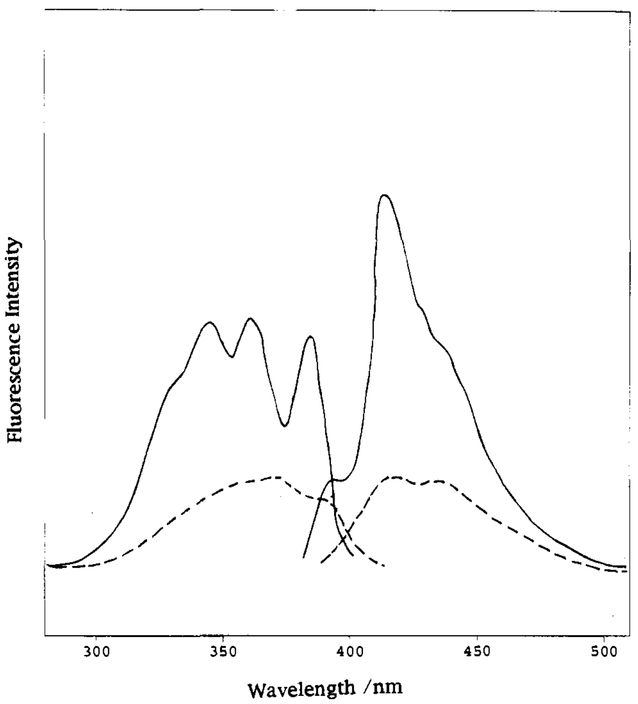

Figure 5. Fluorescence emission and excitation spectra of *Z*-**1** in dichloromethane solution at room temperature (- - -) and at 77 K in an EPA glass (—).

than the reported values; however, this does not alter the conclusion that fluorescence decay displays both a long-lived and short-lived component. The preexponentials determined for the long-lived and short-lived fluorescence can be used to calculate the percent of the total fluorescence arising from each component (Table 3).[13] The contribution of the long-lived component is observed to decrease with increasing solvent polarity from 89% in benzene to 18% in EPA.

The temperature dependence of the fluorescence decay of *E*-**1** was investigated in diethyl ether solution. The lifetime of the long-lived component increases from 2.7 ns at 298 °C to 3.4 ns at 190 °C. The lifetime of the short-lived component increases from 0.4 to 1.3 ns over the same temperature range. The contribution of the long-lived component to the total fluorescence decreases from 69% to 10% over this temperature range.

No fluorescence is detected from *Z*-**1** in methylcyclohexane or benzene solution at room temperature or at 77 K in a methylcyclohexane glass. Very weak ($\Phi_f < 0.01$) fluorescence is observed for *Z*-**1** in dichloromethane solution (Figure 5). Both the excitation and emission spectra display some structure, whereas the absorption spectrum (Figure 1) does not. Weaker fluorescence is observed in dimethyl sulfoxide and ethanol solution. The emission maximum (ca. 435 nm) is the same in all three solvents. The fluorescence decay of *Z*-**1** in dichloromethane solution is monoexponential (τ = 2.2 ns), whereas that of *E*-**1** is biexponential (Table 3). The fluorescence emission and excitation spectra of *Z*-**1** in an EPA glass at 77 K are shown in Figure 5. The vibrational structure is similar to that observed for *E*-**1** (Figure 4); however, the maxima are at slightly longer wavelength than those of *E*-**1** and are independent of excitation wavelength. Thus neither the room temperature nor the 77 K fluorescence of *Z*-**1** can be attributed to *E*-**1** present as an impurity.

Fluorescence quantum yields and lifetimes for *E*-**2** in benzene and ethanol solution are also reported in Table 3. These values are independent of excitation wavelength, as is the appearance of the fluorescence spectrum. The lifetime of *E*-**2** is similar to that of the long-lived component of the fluorescence of *E*-**1**. The weak fluorescence detected for solutions of *Z*-**2** containing a 2–3% impurity of *E*-**2** can be attributed to the impurity. Thus *Z*-**2** is either very weakly fluorescent or nonfluorescent.

Table 4. Photoisomerization Quantum Yields and Steady States

reactant	solvent	λ_{ex}, nm	$\Phi_{E,Z}$	$\Phi_{Z,E}$	% Z^a
1	benzene	366	0.21		>99
	diethyl ether	366	0.45		>99
		392	0.12		>99
	dichloromethane	366	0.52		>99
	ethanol	366	0.61		>99
		420			>99
	DMSO	366			>99
		420			40
2	benzene	366	0.12	0.11	*b*
	ethanol	366	0.12	0.11	*b*

[a] Isomer content obtained upon prolonged irradiation of either isomer. [b] Degradation occurred prior to reaching steady state.

Photoisomerization. Quantum yields for photoisomerization of *E*-**1** (Φ_i) in several solvents are reported in Table 4. The value of Φ_i is lower in benzene than in more polar solvents. The value of Φ_i in diethyl ether solution is distinctly lower for excitation in the long wavelength tail of the absorption band (392 nm) than at 366 or 254 nm. Quantum yields for isomerization of *Z*-**1** at room temperature using 366 nm irradiation are too low for accurate measurement ($<10^{-3}$) in all solvents investigated. Irradiation of either isomer at 366 nm results in isomer mixtures containing >99% *Z*-**1**. Irradiation of *Z*-**1** at 420 nm in dimethyl sulfoxide solution results in slow conversion to a nonequilibrium mixture containing 60% *E*-**1**. The incident light is absorbed more efficiently by *Z*-**1** than by *E*-**1** under these conditions. Irradiation of *Z*-**1** at 420 nm in dichloromethane solution at 40 °C, but not at room temperature, also results in isomerization.

Quantum yields for photoisomerization of *E*-**2** and *Z*-**2** in benzene and ethanol solution are also reported in Table 4. Similar values were obtained for both isomers in both solvents. Photostationary states could not be determined due to the competition of photodecomposition with photoisomerization.

Discussion

The photochemical behavior of the *E* and *Z* isomers of 2-(2-(2-pyridyl)ethenyl)indole is notable in several respects. The observation of dual exponential fluorescence decay of *E*-**1** suggests the presence of at least two excited state conformers of substantially different lifetime and polarity and provides the framework for analysis of the pronounced solvent, wavelength, and temperature dependence of the photochemical behavior of *E*-**1**. This analysis leads to the conclusion that one fluorescent conformer is significantly more reactive toward singlet state isomerization than is the other. In contrast *Z*-**1** exists predominantly as a single conformer in which the indole N–H is hydrogen bonded to the pyridyl nitrogen. This hydrogen bond persists even in highly polar solvents and evidently is responsible for the absence of photoisomerization.[1,2] A minor conformer of *Z*-**1** may be responsible for its weak fluorescence in polar solvents.

Ground State Conformers of *E*-1. On the basis of analogy to related diarylethylenes[8] we tentatively assign the dual fluorescence of *E*-**1** to conformers *E*-**1a** and *E*-**1b** (Chart 2). It is, of course, possible that a significant population of a third (and even fourth) conformer is present and that its singlet state is either nonfluorescent or has a fluorescence lifetime similar to that of one of the other fluorescent comformers. While we

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[13] Birks, J. B.; Bartocci, G.; Aloisi, G. G.; Dellonte, S.; Barigelletti, F. *Chem. Phys.* **1980**, *51*, 113.

cannot exclude this possibility, our results are fully consistent with the presence of only two conformers.

The fluorescence emission and excitation spectra of *E*-**1** in benzene solution (Figure 3) indicate that one conformer absorbs and emits at slightly longer wavelength than the other. The lowest energy electronic transition of *E*-**1b**, as calculated by the ZINDO algorithm, is at lower energy that that of *E*-**1a** (Table 2). This calculated difference is qualitatively consistent with the appearance of the frontier orbitals (Figure 2) which resemble those of a *s-cis* diene in the case of *E*-**1b** and a *s-trans* diene in the case of *E*-**1a**.[14] On this basis we assign *E*-**1b** as the conformer absorbing and emitting at longer wavelength and *E*-**1a** at shorter wavelength. Since long-wavelength excitation of *E*-**1** in benzene solution results only in the observation of long-lived fluorescence, we can further assign the long-lived fluorescence to *E*-**1b** and the short-lived fluorescence to *E*-**1a**. It should be possible to fully resolve the absorption and fluorescence spectra of *E*-**1a** and *E*-**1b** by means of principal component analysis;[15] however, we have not as yet attempted to do so. Support for the assignment of *E*-**1b** as the conformer absorbing and emitting at longer wavelength and with the longer fluorescence lifetime is provided by comparisons with the *N*-methyl derivative *E*-**2**. The increased steric demand of $\mathrm{N{-}CH_3}$ vs N−H should favor the *s-trans,cis* vs *s-cis,cis* conformer of *E*-**2**. The similar fluorescence maxima, lifetimes, and quantum yields (*vide infra*) for the long-lived conformer *E*-**1b** and *E*-**2** suggest that they are structurally related.

The ZINDO electronic structure calculations also provide dipole moments for the conformers of *E*-**1**. The calculated dipole moment of *E*-**1b** is significantly smaller than that of *E*-**1a** (Table 2), thus providing a possible explanation for the solvent dependence of the ^{1}H NMR chemical shifts and photochemical behavior of *E*-**1**. Increasing solvent polarity would be expected to shift the conformational equilibrium in the direction of the more polar conformer *E*-**1a**. Shim et al.[16] have previously proposed that the ratio of *s-cis*/*s-trans* conformers for *E*-2-styrylquinoline is solvent dependent as a consequence of different dipole moments for the two rotamers. This proposal is in qualitative agreement with the observation that the fluorescence decay of *E*-**1** is dominated by the long-lived component (attributed to *E*-**1b**) in benzene solution and by the short-lived component (attributed to *E*-**1a**) in EPA or DMSO solution (Table 3). Since the two conformers do not have the same extinction coefficients or fluorescence quantum yield (vide infra) their ground state populations cannot be directly determined from the preexponentials for fluorescence decay.

Photochemical Behavior of the Conformers of *E*-1. Irradiation of *E*-**1** results in the observation of fluorescence and photoisomerization with quantum yields which are dependent upon solvent and excitation wavelength (Tables 3 and 4). Photoisomerization might occur via either the initially populated singlet state or intersystem crossing to the triplet. The behavior of the triplet states of *E*-**1** and *Z*-**1** generated by biacetyl sensitization has been investigated in one of our laboratories[2] and differs markedly from that of the singlet state. Whereas the singlet state of *Z*-**1** fails to undergo photoisomerization, the triplet state undergoes an efficient, quantum-chain isomerization reaction. It is, of course, possible that *E*-**1** undergoes intersystem crossing but *Z*-**1** does not. However, as discussed below, our results indicate that the isomerization of *E*-**1** is a singlet state process.

Table 5. Ground and Excited State Properties of Confomers

	E-**1a**	*E*-**1b**	*Z*-**1a**	*Z*-**1b**
$\tau_{s,\,ns}$	0.4	2.5	<0.01	2.2
Φ_f	0.04 ± 0.02	0.50 ± 0.05	<0.001	
k_f, $\times 10^{-8}\ s^{-1}$	1.0	2.0		
Φ_i	0.64 ± 0.03	0.10 ± 0.02	<0.01	
k_i, $\times 10^{-8}\ s^{-1}$	16	0.4		
ΔG°, kcal/mol[a]	0.6	0.2	(0)	>1.5
E_s, kcal/mol[b]	73	70	68	73

[a] Free energies relative to **Z-1a** estimated from experimental data in nonpolar solvents. [b] Singlet energies estimated from fluorescence data or ZINDO calculations.

The two confomers *E*-**1a** and *E*-**1b** are in rapid equilibrium in the ground state; however, their singlet excited states do not equilibrate (NEER principle[17]). The singlet state behavior of the two conformers can be distinguished on the basis of the results obtained for excitation wavelength and solvent dependence. Irradiation of *E*-**1** at long wavelengths (> 390 nm) in nonpolar solvents (benzene or ether) results in selective excitation of conformer *E*-**1b**, as evidenced by the observation of single exponential fluorescence decay. The fluorescence and isomerization quantum yields for *E*-**1** under these conditions are similar to those for *E*-**2** (Tables 3 and 4). Thus we can assign approximate values of $\Phi_f = 0.5 \pm 0.05$ and $\Phi_i = 0.1 \pm 0.02$ for the conformer *E*-**1b** in nonpolar solvents. Since the singlet lifetime, Φ_f, and Φ_i for *E*-**2** are not strongly solvent dependent, we assume that the same is true for the conformers *E*-**1a** and *E*-**1b**, which have similar lifetimes in several solvents (Table 3). Thus the solvent dependence of the values of Φ_f and Φ_i (Tables 3 and 4) is attributed to a change in ground state populations. The low value of Φ_f and high value of Φ_i observed in ethanol solution indicate that *E*-**1a** is the predominant conformer in this solvent, in accord with fluorescence decay measurements. On the assumption that 366 nm excitation of *E*-**1** in ethanol results in 90−95% population of conformer *E*-**1a**, values of $\Phi_f = 0.04 \pm 0.01$ and $\Phi_i = 0.64 \pm 0.03$ can be calculated for *E*-**1a**. Similar analysis provides an estimated 25−30% population of conformer *E*-**1a** in benzene solution.

The estimated values of Φ_f and Φ_i for conformers *E*-**1a** and *E*-**1b** are reported in Table 5 along with the average of the singlet lifetimes for these conformers in several solvents. Rate constants for fluorescence and isomerization can be calculated from the estimated quantum yields and average lifetimes of the two conformers ($k = \Phi\tau^{-1}$). The calculated values of k_f for the two conformers are similar, as expected since the lowest singlets have the same configuration and similar oscillator strengths. Similar results have been reported by Mazzucato et al.[18] for the conformers of (*E*)-2-naphthyl-3′-pyridylethylene. In contrast, the two conformers of 2-napthylphenylethylene have different singlet state configurations and different fluorescence rate constants.[15] The values of k_f for both conformers of *E*-**1** are relatively large for a 1,2-diarylethylene, in accord with the large calculated oscillator strengths for the lowest singlet states (Table 2). Whereas the calculated values of k_f are similar for *E*-**1a** and *E*-**1b**, the values of k_i differ by a factor of 40 (Table 5). Mazzucato et al.[18] attributed the difference in lifetimes for the short-lived and long-lived conformers of (*E*)-2-naphthyl-3′-pyridylethylene to more rapid internal rotation in the short-lived conformer; however, the difference in conformer lifetimes ($\tau_a/\tau_b \sim 3$) is much smaller than that for *E*-**1**.

The remarkable difference in the photochemical behavior of *E*-**1a** vs *E*-**1b** is further illustrated by the Arrhenius plots for

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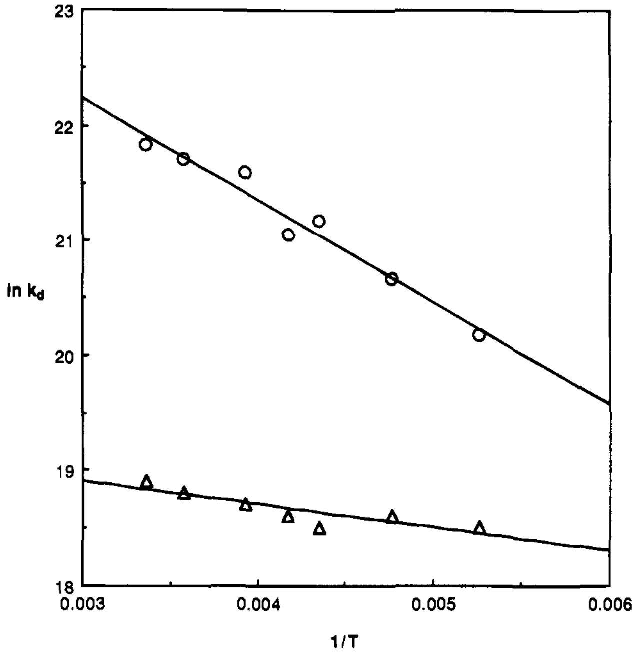

Figure 6. Arrhenius plots of the temperature dependence of the nonradiative decay rate constants for *E*-**1a** (○) *E*-**1b** (△).

singlet state nonradiative decay ($k_d = \tau^{-1} - k_f$) shown in Figure 6. The Arrhenius plot for *E*-**1a**, in which isomerization is the predominant pathway for nonradiative decay, yields values of $E_{act} = 1.8$ kcal/mol and $\log A = 10.8$. Both the activation energy and preexponential are unusually small for isomerization of a diarylethylene.[7] The Arrhenius plot for *E*-**1b**, in which internal conversion is presumably the predominant nonradiative decay pathway, has a much smaller slope and intercept than does the plot for *E*-**1a**. The failure of singlet state isomerization of *E*-**1b** to compete with radiative and nonradiative decay may result from either a large barrier for twisting on the singlet state surface or a small preexponential which might arise from crossing between states of substantially different character.

Ground State Conformers of Z-1. Our earlier investigation of the ground state conformation of *Z*-**3** by means of ^{1}H NMR NOE studies led to the conclusion that it exists predominantly in a hydrogen-bonded conformation in $CDCl_3$ solution but not in DMSO-d_6 solution.[3] Since photoisomerization of *Z*-**3** is observed only in DMSO and other solvents capable of disrupting the intramolecular hydrogen bond, the absence of photoisomerization in nonpolar solvents was attributed to the intramolecular hydrogen bond. NOE studies of *Z*-**1** indicate that *Z*-**1a** (Chart 2) is the major conformer in both $CDCl_3$ and DMSO solution. This result does not preclude the presence of a minor conformer in both solvents. While a strong hydrogen-bond acceptor such as DMSO might have been expected to disrupt the intramolecular hydrogen bond in *Z*-**1a**, the large calculated dipole moment of *Z*-**1a** (Table 2) may account for its existence as the major conformer in polar as well as nonpolar solvents. We have not investigated the conformation of the *N*-methyl derivative *Z*-**2**, but we expect it is the same as that of the minor conformer *Z*-**1b**.

Ground state equilibration of *E*-**1** and *Z*-**1** by means of reversible addition of the phenyl selenyl radical[9b] indicates that *Z*-**1** is slightly more stable (ca. 0.2 kcal/mol) than *E*-**1** in benzene, but less stable in diethyl ether (ca. 0.4 kcal/mol). Equilibration of *E*-**2** and *Z*-**2** in benzene solution indicates that *E*-**2** is more stable by ca. 2 kcal/mol. On this basis, the estimated strength of the intramolecular hydrogen bond is >2 kcal/mol in nonpolar solvents. The slightly lower energy of *Z*-**1** vs *E*-**1** in nonpolar solvent is similar to the result obtained for *Z*-**4** vs *E*-**4**.[4] In the solid state *Z*-**1** is 6.9 kcal/mol more stable than *E*-**1** as determined by DSC measurements.[2] By analogy to the solid state structures of *E*-**3** and *Z*-**3**, it is probable that chains or stacks of molecules are assembled via intermolecular hydrogen bonding.[3] Thus the solid state structures of *E*-**1** and *Z*-**1** may be very different than their solution structures.

Photochemical Behavior of Z-1. The absence of isomerization upon direct irradiation of *Z*-**1** and its occurrence upon triplet sensitization indicates that the lowest singlet of *Z*-**1** undergoes neither isomerization nor intersystem crossing. Its *N*-methylated analog *Z*-**2** undergoes moderately efficient photoisomerization in both nonpolar and polar solvents (Table 4). No fluorescence is observed for *Z*-**1** in the nonpolar solvents benzene and methylcyclohexane and in a glass of the latter solvent at 77 K. The weak structureless fluorescence observed for *Z*-**1** in several more polar solvents and the structured fluorescence in an EPA glass at 77 K (Figure 5) might be attributed to either the hydrogen-bonded conformer *Z*-**1a** or a low equilibrium concentration of *Z*-**1b**. The former explanation appears to be inconsistent with the relatively long fluorescence lifetime measured in dichloromethane solution (2.2 ns). This lifetime and the low fluorescence quantum yield (<0.001) would require a fluorescence rate constant of $k_f < 10^6$ s^{-1}, substantially lower than the values for *E*-**1a** or *E*-**1b** (Table 5) and of other 1,2-diarylethylenes.[7] The latter explanation is consistent with both the anticipated solvent effect upon conformational equilibria and the low fluorescence quantum yield. It is also consistent with the higher energy of the onset of room temperature fluorescence vs absorption (Figures 1 and 5). The non-hydrogen-bonded conformer *Z*-**1b** would be expected to be less planar and thus have a higher singlet energy and lower extinction coefficient than *Z*-**1a**, as is observed for *Z*-**2** (Table 1). The efficiency of photoisomerization of *Z*-**1b** would be expected to be similar to that of *Z*-**2** ($\Phi_i = 0.11$). Thus the absence of measurable photoisomerization for *Z*-**1** requires that the population of *Z*-**1b** be <10% in both polar and nonpolar solvents.

The absence of photoisomerization of *Z*-**1a**[2] and of *Z*-**3**[3] in nonpolar solvents has been attributed to a hydrogen bond-induced barrier for twisting about the ethylene bond in the singlet state. The observation of photoisomerization at elevated temperatures is consistent with this proposal.[3] However, elevated temperature might also increase the population of reactive, non-hydrogen-bonded conformers. A large barrier for twisting would be expected to result in the observation of fluorescence or intersystem crossing, as is the case for singlet styrenes.[19] However, no fluorescence or intersystem crossing is observed for *Z*-**1a** or *Z*-**3**.[3] In the case of *Z*-**5** and *Z*-**6**, adiabatic intramolecular hydrogen transfer to yield the fluorescent tautomers **5′** and **6′** has been observed to compete effectively with isomerization.[5b,6] The ground state of **6′** can be observed by transient absorption spectroscopy and undergoes return hydrogen transfer with a rate constant of 2.1×10^6 s^{-1} at 16 °C, whereas the ground state of **5′** has not been detected. While we have not observed the analogous tautomer of *Z*-**1a**, it is possible that the excited tautomer is nonfluorescent and that the ground state tautomer rapidly reverts to *Z*-**1a**.[20] Alternatively, the N–H stretch may serve as an accepting mode for the nonradiative decay of *Z*-**1a**, resulting in rapid nonradiative decay without complete hydrogen transfer.[21] ZINDO calculations predict that a n → π^* transition lies at slightly higher

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energy than the allowed $\pi \rightarrow \pi^*$ transition of *Z*-**1a**. Inversion of this order resulting from some combination of geometric relaxation, solvation, or computational inaccuaracy could explain the absence of fluorescence and the involvement of the intramolecular hydrogen bond in nonradiative decay.

Concluding Remarks. The photochemical behavior of *E*-**1** and *Z*-**1** is highly dependent upon the identity of the ground state conformer. The barrier for singlet state isomerization of conformer *E*-**1a** is relatively low, resulting in a short singlet lifetime and high quantum yield for isomerization. The barrier for isomerization of conformer *E*-**1b** is higher, resulting in a longer singlet lifetime and low quantum yield for isomerization. The singlet state of conformer *Z*-**1a** does not undergo isomerization at room temperature, as a consequence of either a large barrier for isomerization or rapid nonradiative decay. The ground state population of conformer *Z*-**1b** is too low to permit determination of its isomerization efficiency.

The barrier for singlet state isomerization of arylethylenes is usually associated with a surface crossing involving the lowest singlet state and a higher energy singlet state.[22] Crossing this barrier leads to a perpendicular singlet which can decay to both the *E* and *Z* ground states. It is interesting to note that configurational isomerization of *E*-**1a** without concomitant conformational isomerization would result in the formation of *Z*-**1a**, whereas the configurational isomerization of *E*-**1b** would result in the formation of *Z*-**1b**. The energetics of singlet state configurational isomerization can be discussed using the relative ground state energies and singlet energies summarized in Table 5. The ground state energies are those obtained from our experimental studies in nonpolar solvents. The singlet energies are obtained from the fluorescence 0,0 bands except for *Z*-**1a** whose singlet energy is estimated from its calculated singlet energy relative to that for *E*-**1a** (Table 2). On the basis of these estimated ground and excited state energies, the energy of singlet *E*-**1a** is ca. 5.6 kcal/mol above that for *Z*-**1a**, whereas the energy of singlet *E*-**1b** is >4 kcal/mol beneath that for *Z*-**1b**. This difference in energetics could account for the smaller barrier for twisting in singlet *E*-**1a** vs *E*-**1b**.

Experimental Section

^{1}H NMR spectra were recorded on Gemini 300 or 400 MHz spectrophotometers in CDCl$_3$ or DMSO-d_6 with TMS as an internal standard. Product ratios were analyzed with a Hewlett-Packard 5890 A chromatograph equipped with a 10 m × 0.53 mm capillary column. UV−visible absorption spectra were measured with a Hewlett-Packard Model 8452A diode array spectrophotometer in 1 cm path length quartz cuvettes. Room temperature emission and excitation spectra of solutions stoppered with white rubber septa (Aldrich) and purged with nitrogen for >5 min were recorded using a Perkin-Elmer Model 286 double beam spectrophotometer in 1 cm path length quartz cells. Fluorescence quantum yields were determined relative to 2,5-bis[5-*tert*-butylbenzoxazolyl-(2)]thiophene ($\Phi_f = 0.74$ in cyclohexane[23]). Solutions were approximately 5×10^{-4} M and purged with nitrogen for >5 min in 1 cm path length quartz cuvettes or quartz EPR tubes. Fluorescent lifetimes were measured with a PTI LS-1 spectrophotometer using a gated hydrogen arc lamp and single photon counting techniques. The decays were deconvoluted using a single multiexponential least-squares analysis. The reduced χ^2 values, randomness of the residuals, and autocorrelation functions were used to determine the goodness of the fit. Low-temperature emission spectra and fluorescent lifetimes were obtained using a liquid nitrogen cooled fluorescence dewar with a hanging finger window or an Oxford Instruments variable-temperature liquid nitrogen cryostat Model DN1704 equipped with a Model ITC4 temperature controller.

The light sources for photostationary state measurements were a Hanovia 450-W high-pressure mercury arc lamp with merry-go-round apparatus and Corning glass filters 7-54 and 0-52 (366 nm) or a Rayonet reactor equipped with 254 or 420 nm lamps. The light source for quantum yield measurements was an optical bench equipped with a 200-W high-pressure Oriel mercury−xenon lamp, a Bausch and Lomb high-intensity monochromator, and a thermostated cell holder equipped with a magnetic stirrer.

Photochemical equilibria and quantum yields were determined in triplicate for 2 mL aliquots of approximately 0.005 M solution contained in quartz cuvettes. Solutions were purged for >5 min with dry nitrogen prior to irradiation and stirred during irradiation. Quantum yields were determined at <10% conversion using 254 nm irradiation with *E*-stilbene isomerization as the actinometer.[24] Aberchrome 540 was used as an actinometer at 366 nm[25] and ferrioxalate actinometry at 392 nm.[26] Ground state thermal equilibria for *E*-**1** and *Z*-**1** (and for *E*-**2** and *Z*-**2**) were determined by irradiating 0.006 M diphenyl diselenide in diethyl ether at 420 nm in the presence of either 0.006 M *Z*-**1**, 0.003 M *Z*-**1**, or 0.006 M *E*-**1**.[10b]

INDO/S-SCF-CI (ZINDO) calculations were performed using the method developed by Zerner and co-workers[11a−c] and implemented as described by Lewis et al.[11d] The geometries for *E*-**1a**, *E*-**1b**, and *Z*-**1a** were assumed to be the minimum energy conformations as determined by MAXIMIN2.[9] The ZINDO calculations were performed on a Stellar mini supercomputer and required approximately 5−10 min of CPU time.

Solvents were spectral grade (Aldrich or Fisher). Dichloromethane was distilled over calcium hydride prior to use. Benzene was distilled over sodium prior to use. Methyl alcohol was used as received. Dimethyl sulfoxide was distilled over NaNH$_2$. (*E*)-Stilbene (Aldrich) was recrystallized two times from benzene and once from ethyl alcohol. All other compounds were used as received. The 2-(2-(2-pyridyl)-ethenyl)indoles (*E*-**1** and *Z*-**1**) were prepared by the method of Snieckus and co-workers.[1] *Z*-**1**: Mp 113−114 °C (lit.[1] mp 118 °C). *E*-**1**: Mp Sbl 170 °C (lit.[1] mp 210−211 °C). The *N*-methyl derivatives *E*-**2** and *Z*-**2** were prepared using a modification of the method of Snieckus and co-workers[1] and have spectral properties similar to those previously reported.

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