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Relaxation Pathways of Photoexcited Diaminostilbenes. The *meta*-Amino Effect

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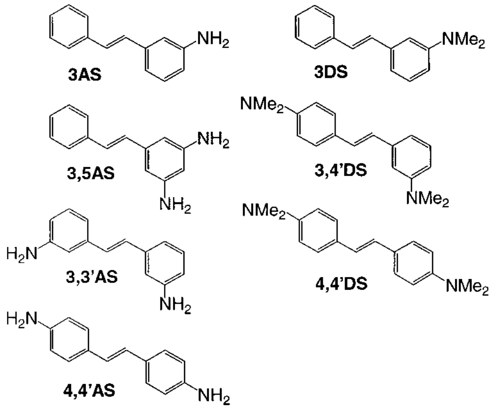
The spectroscopy and photochemistry of several 3-substituted *trans*-diaminostilbenes have been investigated and the results compared with those from previous studies of 4,4′-diaminostilbenes. The excited-state properties of 3,5-diaminostilbene and 3,3′-diaminostilbene are similar to those for the parent 3-aminostilbene. These amines display long, temperature-independent singlet lifetimes and large fluorescence quantum yields. The long singlet lifetimes are a consequence of large barriers for torsion about the central double bond on the singlet state surface and low fluorescence rate constants. Thus, these diaminostilbenes display the "*meta*-amino effect" previously identified for 3-aminostilbene and for some amine-donor−acceptor substituted stilbenes. The 4,4′-diaminostilbenes also have larger torsional barriers in nonpolar solvents but shorter singlet lifetimes as a consequence of larger fluorescence and intersystem crossing rate constants. The photophysical properties of 3,4′-dimethylaminostilbene are similar to those of 4,4′-aminostilbenes; however, it has a lower torsional barrier, similar to that of the parent 4-aminostilbene.

Introduction

The presence of a *meta*-amino substituent exerts a profound effect upon the photochemistry of *trans*- and *cis*-stilbene.[1−3] For example, *trans*-3-aminostilbene (3AS, Chart 1) has a substantially longer singlet lifetime, larger fluorescence quantum yield, and smaller isomerization quantum yield than either unsubstituted *trans*-stilbene or unsubstituted *trans*-4-aminostilbene.[2] The origin of this difference in behavior, which we have called the "*meta*-amino effect", lies in an unusually large barrier for torsion about the central stilbene double bond on the excited singlet state energy surface. Whereas the 4-amino substituent lowers the energies of both the planar twisted stilbene singlet states, the 3-aminosubstituent lowers the energy of the singlet state more than it lowers the twisted state, resulting in a larger torsional barrier. Similar differences in lifetime and reactivity have been observed for 3- versus 4-*N*,*N*-dimethylaminostilbene (3DS) and for derivatives of styrylnaphthalenes, styrylpyridines, and donor−acceptor substituted stilbenes.[1,3]

The photochemistry of 4,4′-diaminostilbene and its tetramethyl derivative (4,4′AS and 4,4′DS, Chart 1) has been the subject of several investigations.[4−8] The singlet lifetimes of these molecules in nonpolar solvents are among the longest observed for a 4,4′-disubstituted stilbene (ca. 1.0 ns) but shorter than that of 3AS. A decrease in the 4,4′AS singlet lifetime with increasing solvent polarity has been attributed to a decrease in the barrier for singlet state torsion.[4] These reports prompted us to investigate the excited-state properties of several isomers of *trans*-diaminostilbene which possess *meta*-amino substituents (Chart 1). We report here our results for 3,5-diaminostilbene (3,5AS), 3,3′-diaminostilbene (3,3′AS), and 3,4′-dimethylaminostilbene (3,4′DS). The behavior of these molecules will be compared to that of both the monoaminostilbenes and the diaminostilbenes 4,4′AS and 4,4′DS.

CHART 1



Experimental Section

Materials. The nitrostilbenes were synthesized by means of Wittig reactions[9] from the corresponding nitrobenzaldehyde and triphenylphosphonium chloride in a dichoromethane/water (50% in K_2CO_3) system with tetrabutylammonium iodide as phase-transfer catalyst (10 mol %). The nitrostilbenes were purified by column chromatography on silica gel using dichoromethane as eluent. The trans isomer was enriched by refluxing the mixture of the isomers in benzene using catalytic amounts of iodine. The aminostilbenes were obtained from the nitro derivatives by reduction with Zn/HCl−CH_3COOH.[10] 3,4′DS was obtained by subsequent methylation with formaldehyde/cyanoborohydride.[11] The aminostilbenes were purified by column chromatography on silica gel (230−400mesh) 3,5AS:dichloromethane−methanol (90:10), 3,4′DS: hexanes−EtOAc (95:5). The purity of *trans*-3,5AS, *trans*-3,3′AS, and *trans*-3,4′DS was estimated to be >98.5% on the basis of GC analysis. Their identity was confirmed by ^{1}H NMR. All solvents for spectroscopic measurements were of Aldrich photospectrometric grade quality and used as received. 2-Methyltetrahydrofuran (Aldrich) was distilled from Na prior to use.

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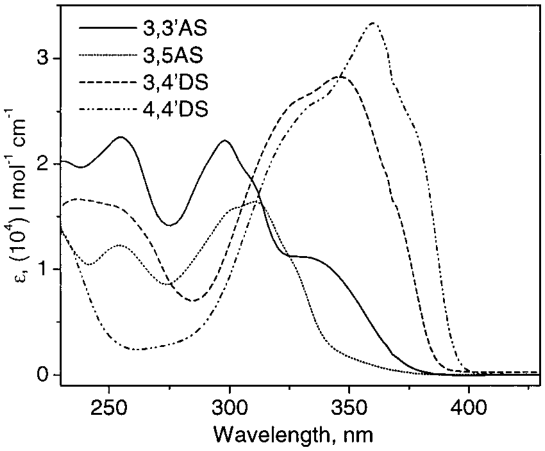


Figure 1. UV Absorption spectra of 3,3′AS, 3,5AS, 3,4′DS, and 4,4′DS in methylcyclohexane.

TABLE 1: Maxima of UV Absorption (λ_{abs}) and Fluorescence (λ_{fl}), Fluorescence-Band Half-Width ($\Delta\nu_{1/2}$) and Stokes Shifts ($\Delta\nu_{st}$) for the Aminostilbenes

compds	solvent[a]	λ_{abs} (nm)	λ_{fl} (nm)	$\Delta\nu_{1/2}$ (cm^{-1})	$\Delta\nu_{st}$ (cm^{-1})[b]
3AS[c]	MC	290, 332[d]	387	4029	4281
	ACN	300, 336[d]	446	3905	7239
3,5AS	MC	310, 356[d]	414	3832	3935
	MT	316, 362[d]	467	3518	6211
	EtOH	312, 362[d]	501	4104	7664
	ACN	312, 362[d]	476	4120	6615
3,3′AS	MC	296, 336[d]	385	4190	3788
	THF	300, 343[d]	429	3698	5844
	EtOH	298, 335[d]	455	3929	7873
	ACN	298, 339[d]	439	4092	6719
4,4′AS[e]	dioxane	351	394, 411		3676
	EtOH	344	414		4915
	ACN	347	409		4368
3DS[f]	MC	298	413	3435	4689
	ACN	342	470	3668	7793
3,4′DS	MC	346	384, 405	2955	3560
	MT	350	418	3451	4978
	EtOH	350	431	3752	5370
	ACN	350	437	3485	5688
4,4′DS	MC	360	393, 415	3152	3026
	ACN[g]	366	422	3626	3434

[a] Methylcyclohexane (MC), 2-methyltetrahydrofuran (MT), acetonitrile (ACN), and ethanol (EtOH). [b] Stokes shifts calculated from the maxima of absorption and emission. [c] Calculated using data from ref 2. [d] Position of shoulder. [e] Data from ref 4. [f] Data from ref 3. [g] Data from ref 7.

Methods. ^{1}H NMR spectra were recorded on a 500 MHz Varian VXR-500 spectrometer. UV spectra were measured on a Hewlett-Packard 8452A diode array spectrometer. Fluorescence spectra were recorded on a SPEX Fluoromax spectrometer. Low-temperature spectra were measured in a Oxford Cryogenics DN1704 cryostat fitted with a ITC4 temperature controller or at 77 K in a Suprasil quartz EPR tube using a quartz liquid nitrogen coldfinger Dewar. Anthracene ($\Phi_{fl} = 0.36$ in cyclohexane)[12] was used as the standard for the fluorescence quantum yield determinations with solvent refractive index correction. The optical density of all solutions was about 0.1 at the wavelength of excitation. All fluorescence spectra are uncorrected, and an error of ±10% is estimated for the fluorescence quantum yields. Fluorescence decays were measured on a single-photon counting apparatus described in detail elsewhere.[2] Quantum yields of photoisomerization were measured at 313 nm using an optical bench equipped with a 200 W Hg (Xe) high-pressure lamp and a monochromator. The optical density of the solutions was > 2. *trans*-Stilbene was used as a reference standard ($\Phi_{tc} = 0.5$ in methylcyclohexane).[13] The extent of photoisomerization (<10%) was determined using HPLC analysis (HP1090, Chromeleon 6.00 (Dionex), Hypersil silica 5 μm, 90:10 hexane:EtOAc). All spectroscopic measurements were performed on solutions that were purged with nitrogen for 20 min. INDO/S-CIS−SCF (ZINDO) calculations were performed on a Macintosh IIfx computer using the ZINDO Hamiltonian as implemented by Cache Release 3.5.[14,15] The structures used in the ZINDO calculations were based on ground state, SCF/AM1, optimized geometries using MOPAC (version 94.10).[15]

Results and Discussion

Absorption Spectra. The absorption spectra of 3,5AS, 3,3′AS, 3,4′DS, and 4,4′DS in methylcyclohexane (MC) solution are shown in Figure 1. The absorption maxima of these compounds in MC and more polar solvents are reported in Table 1 along with data from the literature for 3AS, 3DS, and 4,4′AS. The maxima are relatively insensitive to solvent polarity. This suggests that the ground state and Franck−Condon singlet state have similar dipole moments.

The spectra of 3,4′DS, 4,4′DS, and 4,4′AS display a single broad long-wavelength band similar in appearance to that of *trans*-stilbene or 4-aminostilbene. In the latter two molecules this band is attributed to a π,π^* transition of essentially pure HOMO → LUMO character.[2,16] The red shift caused by the second 4-dimethylamino substituent in 4,4′DS is smaller than that for the first in 4DS ($\lambda_{abs} = 360$, 346, and 294 nm for 4,4′DS, 4DS, and stilbene in alkane solvents). The absorption maximum for 3,4′DS is the same as that for 4DS. Thus, the red shift for 3,4′DS can be attributed entirely to the 4-amino substituent. The red shift for the 4-amino- and 4,4′-diaminostilbenes versus stilbene has been attributed to increased delocalization of the chromophore, the mesomeric effect.[4]

The absorption spectra of 3,5AS and 3,3′AS in MC solution display more complex long-wavelength absorption bands, consisting of a maximum near 300 nm and a longer wavelength shoulder. Their spectra are similar in appearance to those of 3AS,[2] with the shoulder shifted to longer wavelengths for the series 3AS < 3,3′AS < 3,5AS. The maximum is near 300 nm for all of the 3-amino- and diaminostilbenes. The splitting of the long wavelength band of 3AS into a maximum and shoulder has been attributed to configuration interaction resulting from decreased molecular symmetry.[2] The position of the shoulder in 3,3′AS is similar to that of the maximum in 4,4′AS, and the shoulder for 3,5′AS lies at a longer wavelength. Thus band-splitting can result in an even lower energy for the first π,π^* state of 3-aminostilbenes than the mesomeric effect of 4-aminostilbenes.

Fluorescence Spectra. The fluorescence maxima of the aminostilbenes in nonpolar and polar solvents are summarized in Table 1 along with the half-widths of the emission bands ($\Delta\nu_{1/2}$). The spectra of 3,5AS and 3,3′AS are broad and structureless in all solvents, as is the case for 3AS. The spectra of 3,4′DS (Figure 2), 4,4′AS, and 4,4′DS display weak vibronic structure in alkane solvents but are structureless in more polar solvents, as is the case for 4AS or 4DS.[2,3] The fluorescence maxima of all of the aminostilbenes are appreciably red-shifted in more polar solvents, consistent with their assignment to an excited-state possessing charge transfer (CT) character. Band broadening is observed in more polar solvents for all of the diaminostilbenes except 3,3′AS.

The emission spectra are independent of excitation wavelengths for all of the aminostilbenes in all solvents at room temperature, even though the *meta*-aminostilbenes are expected to exist as mixtures of two or more ground-state rotamers.

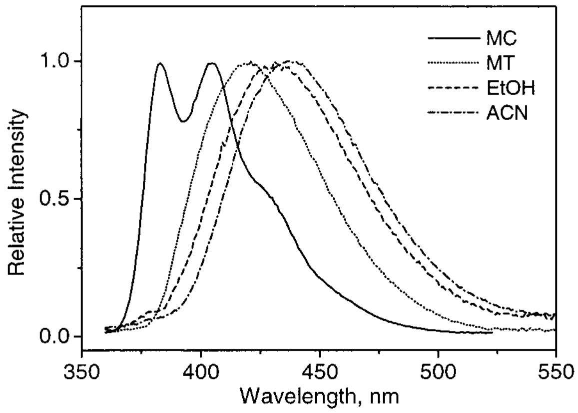


Figure 2. Fluorescence spectra of 3,4′DS in methylcyclohexane, 2-methyltetrahydrofuran, ethanol, and acetonitrile.

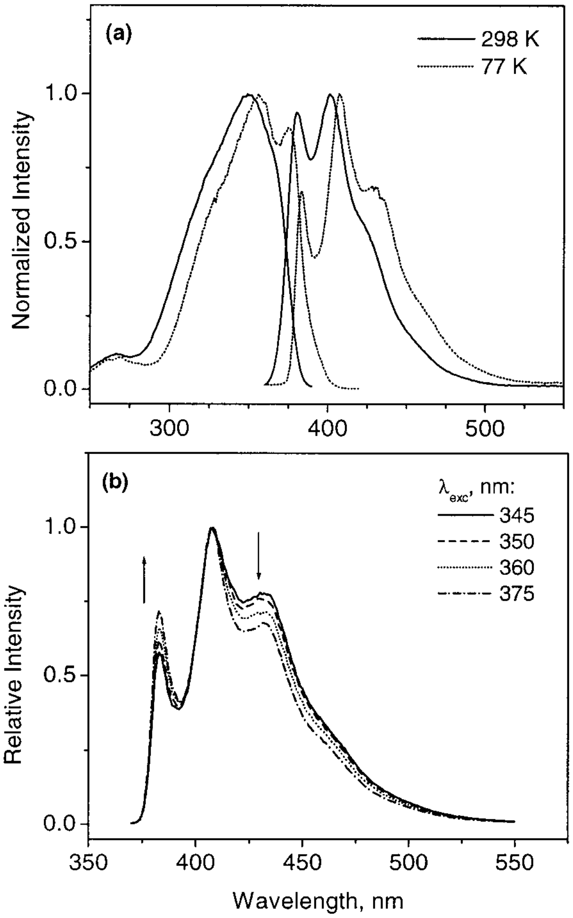


Figure 3. Low-temperature effect for 3,4′DS in isopentane. (a) Comparison of excitation and emission spectra at 298 and 77K. (b) Spectral Shift of the fluorescence spectra by variation of the excitation wavelength at 77 K.

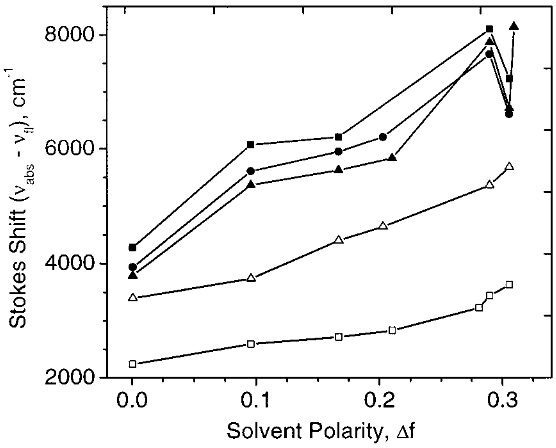


Figure 4. Solvatochromic plot of Stokes shifts for 3AS(■), 3,3′AS (▲), 3,5AS (●), 3,4′DS (△), and 4,4′DS (□). The solvent polarity function corresponds to eq 1.

Furthermore, the room-temperature fluorescence decays are best fit to a single exponential in all cases (vide infra). Thus, either all of the rotamers have similar excitation and emission spectra and decay times, or the emission spectra are dominated by a single rotamer. Evidence for the presence of two fluorescent rotamers with similar spectra is provided by the low-temperature spectra of 3,4′DS in isopentane solution (Figure 3). The 77 K emission spectrum is slightly red-shifted relative to the 298 K spectrum, and both the emission and excitation spectra are better resolved (Figure 3a). Variation of the excitation wavelength results in a change in the relative intensities of the 380 and 430 nm bands when the spectra are normalized at the 405 nm emission maximum (Figure 3b). Analysis of these spectra by means of singular value decomposition with self-modeling[17] provides two nearly identical spectra which differ only in the relative intensities of their vibronic peaks. The assignment of the 77 K emission to two rotamers is supported by the observation of dual exponential fluorescence decay at 77 K (vide infra).

The 77 K emission spectra of the primary diaminostilbenes 3,5AS and 3,3′AS in isopentane solvent are broadened and red-shifted relative to the 298 K spectra (data not shown). These changes are tentatively attributed to aggregation, as proposed for stilbene and other primary aminostilbenes.[3,16,18,19] In the more polar solvents methyltetrahydrofuran and ethanol, the 77 K spectra of all of the diaminostilbenes show no evidence for aggregation and are blue-shifted relative to the 298 K spectra as a consequence of the decrease in solvent polarity which occurs upon freezing.[20]

Solvatochromic Measurements and Dipole Moments. The Stokes shifts, $\Delta\nu_{st}$, for the aminostilbenes, calculated from the maxima of the absorption and fluorescence spectra, are reported in Table 1. The positions of the shoulders in the absorption spectra of the 3-aminostilbenes have been used to estimate their lowest energy transitions. The values of $\Delta\nu_{st}$ increase with increasing solvent polarity. Since only small solvent-induced shifts are observed for the absorption maxima, the solvent dependence of the Stokes shifts is determined largely by the fluorescence maxima. Shown in Figure 4 is a plot of $\Delta\nu_{st}$ versus the solvent parameter Δf (eq 1)

$$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1) \qquad (1)$$

that describes the solvent polarity and polarizability and is calculated from the dielectric constant ϵ and the refractive index n. As previously noted for other primary aminostilbenes, the values of $\Delta\nu_{st}$ for 3,5AS and 3,3′AS do not increase monotonically with Δf, the values for acetonitrile lying below those for the hydroxylic solvents ethanol and methanol.[3] This most likely reflects a specific solvent−solute interaction such as hydrogen bonding or formation of a solvent−solute exciplex.[21]

The dipole moment of the fluorescent CT state, μ^{CT}, can be estimated from a plot fluorescence maxima versus Δf using eq 2

$$\nu_{fl} = -[(^1/_4\pi\epsilon_o)\,(2/hca^3)]\mu_e^{CT}(\mu_e^{CT} - \mu_g^{FC})\Delta f + \text{const}' \qquad (2)$$

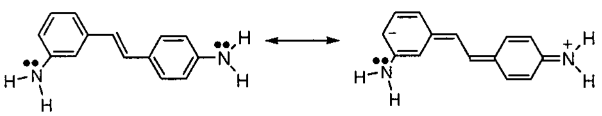
$$m_{fl} = -[(^1/_4\pi\epsilon_o)(2/hca^3)]\mu_e^{CT}(\mu_e^{CT} - \mu_g)$$

TABLE 2: Dipole Moments of the Ground State and the Excited CT State at 298 K Determined from the Solvatochromic Data

compds	μ_g (D)[a]	μ_e^{CT} (D)[b]
3AS[c]	1.5	11.9
3,3′AS	3.08[d]	13.2[d]
3,5AS	0.7	11.5
3DS[e]	1.7	12.1
3,4′DS	2.6[d]	15.0[d]
4,4′DS	2.6	10.6[f]

[a] Calculated by INDO/S-CIS−SCF (ZINDO). [b] Calculated using eq 2 with an Onsager radius of 5 Å for 3,3′AS and 3,5AS, 6 Å for 3,4′DS. [c] Data from ref 2. [d] Slightly different dipole moments have been calculated for ground-state rotamers. The values reported are for the rotamers shown in Chart 1. [e] Data from ref 3. [f] Calculated from data reported in ref 7.

where *a* is the solvent cavity (Onsager) radius.[22,23] Values of the ground-state dipole moment, μ_g, calculated using the ZINDO algorithm are reported in Table 2. The ground-state dipole moments are seen to be modest (<3 D) in all cases. Also reported in Table 2 are the values of μ_e^{CT} obtained from the slope m_{fl} given by the plot of ν_{fl} versus Δf, assuming that $\mu_g^{FC} = \mu_g$. The values of μ_e^{CT} for all of the diaminostilbenes lie in the range 10−15 D. The three rotamers of 3,3′AS and two rotamers or 3,4′DS also have similar values of μ_e^{CT} estimated from their slightly different ground state dipole moments. These values are similar to those for the monoaminostilbenes 3AS, 3DS (Table 2), 4AS, and 4DS and are distinctly smaller than the dipole moments of donor−acceptor substituted stilbenes such as 4-cyano-4′-dimethylaminostilbene and 4-cyano-3′-dimethylaminostilbene (μ_e^{CT} = 21.0 and 21.8 D, respectively).[3,24] The largest value is observed for 3,4′DS. This may reflect more effective charge-resonance stabilization of the planar singlet state (eq 3) than is the case for 4,4′-substitution.



(3)

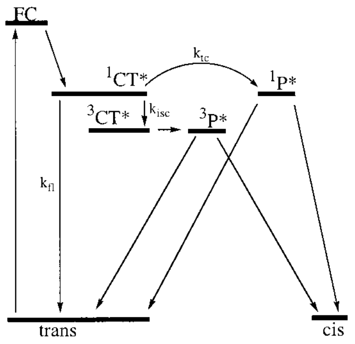
Quantum Yields for Fluorescence and Photoisomerization. Fluorescence quantum yields for the aminostilbenes determined at room temperature in several solvents are reported in Table 3. The values of Φ_{fl} for 3,3′AS in MC and 4,4′AS in dioxane are similar to those for 3AS and 3DS (0.72−0.76) and are among the highest reported to date for unconstrained stilbene derivatives. The values for 3,5AS, 3,4′DS, and 4,4′DS in MC are lower (0.41−0.45) but significantly higher than the values for 4DS or *trans*-stilbene (0.03−0.05).[25] Papper et al.[5] report a value of Φ_{fl} = 0.58 for 4-amino-4′-dimethylaminostilbene in chlorobenzene solution, the largest value for any of the 20 unsymmetrical 4,4′-disubstituted stilbenes investigated. The values of Φ_{fl} for all of the stilbenes in Table 3 decrease with increasing solvent polarity. Smaller values Φ_{fl} are observed for ethanol versus acetonitrile solvent in all cases where these data are available. This effect may be related to the larger Stokes shifts observed in ethanol versus acetonitrile (Table 1 and Figure 4).

TABLE 3: Quantum Yields for Fluorescence and Photoisomerization, Fluorescence Decay Times at 298 and 77 K, Rate Constants for Fluorescence Decay, and the Sum of All Nonradiative Decays in Solvents of Different Polarity

compds	solvent	Φ_{fl}	Φ_{tc}	τ_{fl}^{298K} (ns)	τ_{fl}^{77K} (ns)	k_{fl} (10^8 s^{-1})	k_{nr}[a] (10^8 s^{-1})
3AS	MC	0.75	0.09[b]	7.3	7.2	1.03	0.34
	ACN[b]	0.4	0.23	11.7		0.3	0.55
3,5AS	MC	0.43		23.4	24.7	0.18	0.24
	MT	0.14		18.4	28.9	0.076	0.47
	ACN	0.10		16.1		0.062	0.56
3,3′AS	MC	0.72		6.1	7.9	1.18	0.46
	EtOH	0.24		9.5	15.5	0.25	0.80
	ACN	0.41		12.4		0.33	0.48
4,4′AS[c]	dioxane	0.76	0.10	1.0		7.6	2.4
	EtOH	0.12	0.43	0.30		4.2	30
	ACN	0.30	0.34	0.57		5.2	12
3DS[d]	MC	0.72	0.08	13.0	13.0	0.55	0.21
	ACN	0.20	0.39	13.1		0.15	0.61
3,4′DS	MC	0.41	0.24	1.1	2.4[e]	3.7	5.3
	MT	0.15		1.1	5.7[e]	1.3	7.7
	EtOH	0.08		1.2	6.2[e]	0.66	8.0
	ACN	0.14	0.08	1.2		1.1	7.2
4,4′DS[f]	diethyl ether	0.45		1.2	1.6	3.8	4.6
	EtOH	0.40		0.9	1.7[g]	4.4	6.7

[a] $k_{nr} = 1/\tau(298K) - k_{fl}$ (sum of all nonradiative processes). [b] Data from ref 2, Φ_{tc} in cyclohexane instead of MC. [c] Data from ref 4. [d] Data from ref 3. [e] Lifetime maxima: 3 ns in MC at 120 K, 14 ns in MT at 130 K, and 11 ns in EtOH at 160 K. Short-lived component, τ_{fl} at 77 K: 1.2 ns in MC, 1.7 ns in MT, and 2.04 ns in EtOH. [f] Data from ref 7, Φ_{fl} = 0.39 in *n*-hexane and 0.57 in ACN. [g] Lifetime maximum of 1.8 ns at 200 K.

SCHEME 1: Simplified Scheme for the Deactivation Channels of the Fluorescent $^1CT^*$ State of the *meta*-Aminostilbenes



Quantum yields for trans−cis photoisomerization have been measured for 3,4′DS in MC and ACN solution. These data are reported in Table 3 along with published results for 3AS, 3DS, and 4,4′AS. The isomerization of substituted stilbenes can occur via either a singlet or triplet mechanism, as shown schematically in Scheme 1. Values of Φ_{tc} are larger in polar versus nonpolar solvents except in the case of 3,4′DS, most likely due to a higher contribution of the triplet pathway via intersystem crossing. In either case, torsion about the central double bond yields a twisted intermediate which decays to the ground-state trans and cis isomers with equal probability.[25,26] For most of the aminostilbenes in Table 3 the sum $\Phi_{fl} + 2\Phi_{tc} \approx 1.0$, in accord with fluorescence and singlet or triplet torsion as the dominant modes of excited-state decay. The one exception is the behavior of 3,4′DS in ACN solution for which $\Phi_{fl} + 2\Phi_{tc} \approx 0.3$. This suggests the operation of a nonradiative decay channel that does not result in photoisomerization, as previously observed for several donor−acceptor substituted stilbenes.[3]

Fluorescence Lifetimes. The fluorescence lifetimes of the aminostilbenes at room temperature in several solvents are reported in Table 3. Also reported are the more limited data measured at 77 K in glass-forming solvents. The 23.4 ns decay time of 3,5AS in MC is, to our knowledge, the longest reported for an unconstrained stilbene derivative. Long decay times (>6 ns) are also observed for the 3-substituted monoamines 3AS and 3DS and the diamine 3,3′AS. Shorter decay times (ca. 1 ns) are observed for the 4-substituted diamines 3,4′DS, 4,4′DS, and 4,4′AS. However, even these values are longer than the decay time of *trans*-stilbene, 4AS, or 4DS (ca. 0.1 ns).[2,3]

Increasing solvent polarity results in an increase in lifetime for 3AS and 3,3′AS, little change for 3DS, 3,4′DS, and 4,4′DS, and a decrease in lifetime for 3,5AS and 4,4′AS. Since the decay times are determined by the rate constants for fluorescence and isomerization pathways, the effects of structure and solvent on these processes need to be considered.

Values of the rate constants for fluorescence ($k_{fl} = \Phi_{fl}\tau_{fl}^{-1}$) and total nonradiative decay ($k_{nr} = (1 - \Phi_{fl})\tau_{fl}^{-1}$) are reported in Table 3. Values of k_{fl} in nonpolar solvents are significantly larger for the 4-substituted stilbenes 4,4′AS, 4,4′DS, and 3,4′DS ($k_{fl} > 3 \times 10^8$ s^{-1}) than for the stilbenes which possess only 3-substituents ($k_{fl} < 1 \times 10^8$ s^{-1}). This trend is similar to that observed for the monoaminostilbenes[2] and is consistent with stronger long-wavelength absorption of the 4- versus 3-substituted aminostilbenes (Figure 1). Values of k_{fl} calculated using the Strickler–Berg relationship[27,28] are in good agreement with experimental values obtained using the long-wavelength shoulders of the 3-aminostilbenes.[29] The values of k_{fl} decrease with increasing solvent polarity in most cases. This decrease may result, in part, from the solvent induced shifts of the fluorescence maxima, which result in a decrease in the $\langle\tilde{\nu}\rangle_{av}^{-1}$ term in the Strickler–Berg equation. Solvent-induced changes in the structure of the fluorescent CT state could also result in less favorable Franck–Condon factors for fluorescence.

Values of k_{nr} in nonpolar solvents are also larger for the 4-substituted stilbenes ($k_{nr} > 2.4 \times 10^8$ s^{-1}) than for the 3-substituted stilbenes ($k_{nr} < 0.5 \times 10^8$ s^{-1}). Thus, the long fluorescence lifetime of 3,5AS is a consequence of both slow fluorescence and slow nonradiative decay. The dominant nonradiative decay pathways for most stilbenes are singlet state torsion and intersystem crossing ($k_{nr} = k_{tc} + k_{isc}$, Scheme 1).[25,26] These pathways will be discussed in greater detail the following section. Increasing solvent polarity results in modest increases in k_{nr} in most cases, but more pronounced increases in the case of 4,4′AS.

Temperature Dependence of the Fluorescence Lifetimes. According to Scheme 1, the fluorescence lifetime of the aminostilbenes should be determined, as described in eq 4

$$1/\tau_{fl} = k_{fl} + k_{nr} + A_o e^{(-E_a/RT)} \tag{4}$$

by the rate constants for two unactivated processes, fluorescence (k_{fl}) and intersystem crossing (k_{isc}), and one activated process, torsion about the central double bond on the singlet surface (k_{tc}).

Similar values of τ_{fl} for the diaminostilbenes 3,5AS and 3,3′AS are obtained in MC solution at 298 and 77 K (Table 3). In the case of 3,5AS, lifetimes were also measured at several intermediate temperatures and found to be essentially independent of temperature. The absence of temperature dependence indicates that there is no activated decay process. Intersystem crossing is concluded to be the only nonradiative decay process ($k_{isc} = k_{nr}$), and thus, trans-cis photoisomerization must occur via a triplet state mechanism. The values of k_{isc} for 3,5AS and 3,3′AS in MC are 2.4 and 4.6 × 10^7 s^{-1}, bracketing the value of $k_{isc} = 3.9 \times 10^7$ estimated by Saltiel for stilbene.[25]

The behavior of 3,5AS and 3,3′AS is analogous to that of the monoamines 3AS and 3DS, for which a lower bound of 7 kcal/mol was estimated for the barrier for singlet-state torsion.[2,3] Similar values of $E_a > 7$ kcal/mol can be assumed for 3,5AS and 3,3′AS. In solvents of higher polarity, the lifetime of 3,5AS increases with decreasing temperature. However, the activated process cannot be assigned to singlet-state photoisomerization due to the low value calculated for the preexponential factor derived from the fitting of the temperature dependence of the lifetime ($A_o = 10^{10}$ s^{-1}). Typical A_{tc} values for singlet state isomerization are ca. 10^{12}–10^{14} s^{-1}.[13] Thermally activated intersystem crossing or internal conversion have been discussed as possible explanation for the nature of this activated process.[3]

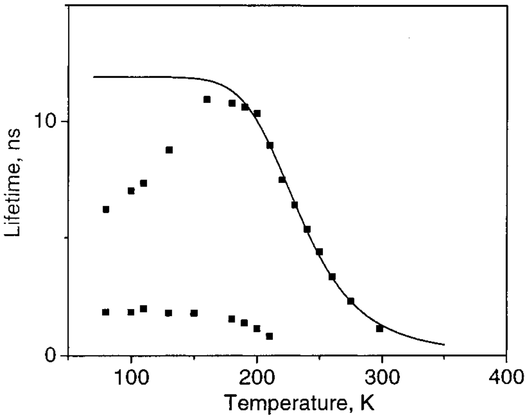


Figure 5. Temperature dependence of the 3,4′DS lifetime in ethanol. The line represents the fit through the high temperature data points using eq 4.

Smit and Ghiggino[4] have estimated the barriers for singlet state torsion of 4,4′AS in several solvents from the temperature dependence of the fluorescence intensity over a relatively small temperature range. They report values of $E_a = 12$ and 3.2 kcal/mol for dioxane and ethanol solution, respectively. Létard et al. have reported that the decay time of 4,4′DS in diethyl ether solution is only slightly dependent upon temperature over the entire range from 77 to 298 K ($\tau = 1.6$ and 1.2 ns, respectively).[7] They attribute the weakly activated process ($E_a < 1$ kcal/mol) to twisting about the phenyl–vinyl bond to yield a fluorescent TICT singlet state; however, increasing solvent viscosity could also account for this modest increase in lifetime.[30] Thus, the values of E_a for double bond torsion may be too large (>5 kcal/mol) to be detected by lifetime measurements at room temperature and below. Analysis of their lifetime data in ethanol solution provides a value of $E_a = 4.9$ kcal/mol, similar to the values for 3,4′DS and 4,4′AS in this solvent. The large torsional barriers for 4,4′AS and 4,4′DS suggest that the predominant channel for nonradiative decay at room temperature in nonpolar solvents is intersystem crossing ($k_{isc} \approx k_{nr}$). The values of k_{nr} reported in Table 3 for these diaminostilbene are ca. 3 × 10^8 s^{-1}, nearly 1 order of magnitude larger than those for stilbene or the 3-aminostilbenes. Thus, the shorter lifetimes for the 4,4′- versus 3,5- or 3,3′-diaminostilbenes result from larger values for k_{fl} and k_{isc}.

The fluorescence lifetime of 3,4′DS in EtOH decreases with decreasing temperature from a value of 1.2 ns at 298 K to a maximum value of 11 ns at 160 K. At lower temperatures, dual exponential fluorescence decay is observed, the decay time of the major, longer-lived component decreasing with decreasing temperature and that of the minor, shorter-lived component increasing with decreasing temperature (Figure 5). The maximum in the decay times of the longer-lived component at 160 K is analogous to the behavior of several other 4-dimethylaminostilbene derivatives.[3,31,32] The origin of this behavior remains the subject of speculation. The observation of dual exponential decay at low temperatures, taken with the observation of excitation-wavelength-dependent emission spectra (Figure 3b), supports the tentative assignment of the two emissions to the two ground-state rotamers of 3,4′DS. The large differences in temperature-dependent decay times would require that the two rotamers have quite different excited-state behavior and that the room-temperature emission be dominated by the longer-lived rotamer. Alternatively, the second component could be an aggregate; however, aggregation is expected to result in a shift or broadening of the fluorescence spectra, which is not observed.[3,19]

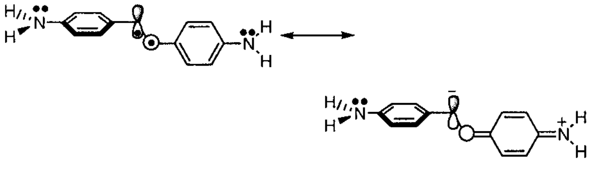
Fitting the lifetime data for 3,4′DS in EtOH (Figure 5) to eq 4 provides a value of $E_a = 4.5$ kcal/mol. A slightly smaller value of $E_a = 3.8$ kcal/mol is obtained from the lifetime data in MC solution. Similar values are obtained from Arrhenius plots of the lifetime data. These values of E_a are somewhat larger than the value of 3.5 kcal/mol for stilbene,[25] contributing to the longer singlet decay time for 3,4′DS versus stilbene. However, they are sufficiently small to suggest that isomerization of 3,4′DS, unlike that of the other diaminostilbenes, occurs predominantly via a singlet state mechanism (Scheme 1, k_{tc}).

Analysis of the Torsional Barriers. The excited-state behavior of the diaminostilbenes 3,5AS and 3,3′AS is analogous to that of the 3-aminostilbenes 3AS and 3DS. For all of these stilbene derivatives, a large barrier for singlet-state torsion results in a long singlet lifetime and high fluorescence quantum yields (Table 3). Photoisomerization occurs via intersystem crossing followed by double bond torsion on the triplet surface. Thus, the diaminostilbenes display the characteristic "*meta*-amino effect" previously observed for the monoamines and donor–acceptor stilbenes possessing 3-amino substituents. The long singlet decay times for the 3-aminostilbenes result not only from the large barrier for singlet torsion, but also from small fluorescence rate constants compared to stilbene or the 4-aminostilbenes (Table 3). The small values of k_{fl} are a consequence of the low oscillator strength of the lowest π,π^* singlet state which results from configuration interaction between several one-electron transitions.

The effects of substituents upon the height of the barrier for singlet state torsion can be analyzed on the basis of the observed effect on the energy of the fluorescent CT singlet state and the anticipated effect on the energy of the twisted intermediate $^1P^*$ (Scheme 1). The singlet energies of all of the diaminostilbenes 3,5AS, 3,3′AS, and 4,4′AS, as determined from the overlap of absorption and emission spectra, are similar, despite the differences in oscillator strength. Michl and Bonaèiæ-Koutecký[33] have described $^1P^*$ for simple alkenes as a resonance hybrid of biradical and charge-transfer configurations (eq 5)

$$\psi_{P}{}^* = c_1\psi_{\mathrm{biradical}(A\cdot B\cdot)} + c_2\psi_{\mathrm{CT}(A^+B^-)} + c_3\psi_{\mathrm{CT}(A^-B^+)} \tag{5}$$

The presence of an electron-donating amino substituent at the para position, but not at the meta position, would be expected to stabilize the charge-transfer configurations and thus lower the energy of $^1P^*$. The large barrier for singlet state torsion of the 3-substituted diaminostilbenes thus results from greater stabilization of $^1CT^*$ versus $^1P^*$, as previously proposed for the parent 3-aminostilbene.[2] The situation for the 4-substituted diaminostilbenes is more complex. Charge separation in a 4,4′-diaminostilbene would place a positive charge adjacent to one aniline ring but a negative charge adjacent to the other, where it would be destabilized by a *para*-amino substituent (eq 6). The net effect would be less stabilizing than a single 4-amino substituent.



(6)

Thus, it is not surprising that the 4,4′-diaminostilbenes have larger barriers for torsion than the parent 4-aminostilbene, at least in nonpolar solvents. In the case of 3,4′DS, the 4-amino substituent stabilizes $^1P^*$ by resonance, whereas the 3-amino substituent should have only a small inductive destabilizing effect. This results in a torsional barrier that is slightly higher than that for the parent 4-aminostilbene (3.8 kcal/mol vs ca. 3.5 kcal/mol), but lower than that for the 4,4′- or 3,3′-diaminostilbenes.

Both $^1CT^*$ and $^1P^*$ have variable charge-transfer character but might be expected to be stabilized to different extents in polar solvents, resulting in a change in the barrier for singlet state torsion. The singlet decay times of 3,5AS and 3,3′AS, like that of 3AS, remain long in polar solvents. Thus, the barrier is high (>7 kcal/mol) in all solvents. In the case of 3,4′DS, the measured barrier is slightly higher in polar versus nonpolar solvent (3.8 kcal/mol in MC vs 4.5 kcal/mol in ethanol). However, in the cases of 4,4′AS and 4,4′DS, the barriers apparently are lower in more polar solvents.[4,6] This suggests that $^1P^*$ is stabilized to a greater extent than $^1CT^*$ in polar solvents.

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