Excited State Properties of Donor−Acceptor Substituted *trans*-Stilbenes: The *meta*-Amino Effect

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The photochemical behavior of 3-dimethylaminostilbene (3DS), 3-amino-3′-cyanostilbene (3A3′CS), and 3-dimethylamino-4′-cyanostilbene (3DCS) has been investigated and compared to that of the analogous 4-amino derivatives. The absorption spectra of the 4-aminostilbenes display a single strong band whereas the spectra of the 3-aminostilbenes display multiple bands or lesser intensity as a consequence of configuration interaction which results from loss of symmetry. The 3-aminostilbenes have substantially higher fluorescence quantum yields and longer fluorescence lifetimes when compared to the 4-aminostilbenes. Based on analysis of the solvatochromic shifts of the absorption and fluorescence spectra, the 3- and 4-aminostilbenes have similar excited state dipole moments which are substantially larger than their ground state dipole moments. The long lifetimes of the 3-aminostilbene charge transfer singlet states are a consequence of low fluorescence rate constants and a large barrier for singlet state torsion. Thus the "*meta*-amino effect" reported previously for 3-aminostilbene is also observed in the case of donor−acceptor substituted stilbenes. In nonpolar solvents the 3-aminostilbenes decay predominantly by fluorescence and intersystem crossing to the triplet state which decays to yield a mixture of trans and cis isomers. In polar solvents a second nonradiative decay channel is operative and is tentatively assigned to internal conversion on the basis of its energy gap dependence. The primary 3-amino-3′-cyanostilbene displays specific solvation in alcohol solvents at room temperature and aggregation in a nonpolar solvent at low temperature.

Introduction

The photochemical behavior of *trans*-stilbene and substituted stilbenes continues to provide a fertile field of investigation.[1−4] Singlet *trans*-stilbene decays via two processes in fluid solution: fluorescence and torsion about the central double bond, leading to formation of a short-lived twisted intermediate which decays to yield a mixture of *trans*- and *cis*-stilbene. The planar singlet is relatively nonpolar and its fluorescence maximum displays only minor solvent-induced shifts; however, the twisted singlet is believed to have zwitterionic character. An increase in polarity upon torsion can account for a decrease in the activation energy for the singlet state isomerization processes with increasing solvent polarity.[2,5,6] A second nonradiative decay process, intersystem crossing, is observed for some substituted stilbenes.[7−9] Stilbene triplets undergo barrierless torsion and thus isomerization can occur via the triplet state as well as the singlet state.[1,10] Substituents can affect both the rate constant for intersystem crossing and the barrier for singlet state torsion.

The excited states of *trans*-stilbenes possessing 4,4′-donor−acceptor substituents such as 4-dimethylamino-4′-cyanostilbene (4DCS) have attracted attention and some controversy.[11−22] The observation of large solvent-induced shifts in the fluorescence, but not the absorption maxima, provided evidence for the charge transfer (CT) character of the fluorescent singlet state. Several models involving multiple singlet states have been proposed for decay of the 4DCS singlet. Prominent among these is twisting about the aniline−cyanostyrene single bond to form a twisted intramolecular charge transfer (TICT) state, analogous to that formed by 4-dimethylaminobenzonitrile (DMABN).[23] However, the fluorescence decay of 4DCS is monoexponential under all conditions of temperature and solvent polarity, unlike the dual exponential decay of DMABN. Recent evidence is consistent with solvent-dependent relaxation of the Franck−Condon (FC) state to either of two CT states.[20] According to this model, the FC state relaxes to an initial CT state within 1 ps. In polar solvents, solvation and geometric relaxation convert the initial CT state to a relaxed CT state which has a longer lifetime and a higher dipole moment than the initial CT state. The lifetime of the relaxed CT state is longer than that of the initial CT state, presumably due an increase in the activation energy for formation of the ^{1}P* state with increasing solvent polarity, opposite the effect of solvent polarity upon the torsional barrier for *trans*-stilbene.[21,22]

Recently, we reported that *trans*-stilbene derivatives possessing a 3-amino substituent have much longer lifetimes and higher fluorescence quantum yields than do their 4-amino isomers.[24,25] This difference in lifetimes is the result of a larger barrier for torsion of the planar singlet state of the 3- vs 4-amino isomer.[25] As a consequence of the higher torsional barrier, 3-aminostilbene undergoes intersystem crossing in competition with fluorescence, leading to photoisomerization via a triplet state mechanism. Preliminary studies of 3-amino-4′-(methoxycarbonyl)stilbene indicated that it also had a much longer singlet decay time than its 4,4′ isomer.[24] Nearly all studies of donor−acceptor substituted stilbenes reported to date have been restricted to 4,4′ derivatives. One exception is a study of 4-dimethylamino-3′-nitrostilbene and its 4,4′ isomer for which similar lifetimes were observed.[17]

In order further define the scope of the "*meta*-amino effect", we have investigated the photochemical behavior of 3-dimethylaminostilbene (3DS) and two donor−acceptor stilbenes, 3-amino-3′-cyanostilbene (3A3′CS) and 3-dimethylamino-4′-cyanostil-

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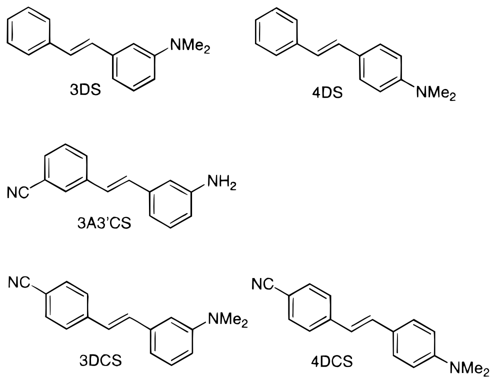

bene (3DCS) (Scheme 1). The spectroscopic properties, the excited state dipole moments, the quantum yields for fluorescence and photoisomerization, and the temperature dependence of the fluorescence decay are presented here and will be discussed in comparison to the para derivatives 4-dimethylaminostilbene (4DS) and 4-dimethylamino-4′-cyanostilbene (4DCS).

Results and Discussion

UV Absorption and Fluorescence Spectra. The absorption spectra of 3DS, 3A3′CS and 3DCS, are shown in Figure 1 along with the spectra of 4DS and 4DCS. The two latter molecules have a single intense band with maxima at 350 and 380 nm, respectively.[11,14,15,26] In contrast, the three former molecules have multiple absorption bands, with the most intense bands having maxima near 300 nm and shoulders of lower intensity between 350 and 370 nm (Table 1). The spectrum of 3DS is similar to that previously observed for *trans*-3-aminostilbene.[25] The multiple transitions of the meta derivatives can be explained by a splitting of the lowest singlet state resulting from configuration interaction due to the loss of symmetry.[25,27] A similar effect has been recently reported for *meta*-DMABN.[28] The energies for the (0−0) transition are nearly identical for the meta and para derivatives (Table 1). The decrease of the $^1S^*$ energy by splitting of the lowest transition due to configuration interactions in the meta case is similar in magnitude to the decrease by the mesomeric stabilization by an amino or an additional acceptor group. The absorption spectra of all the aminostilbenes undergo only small red shifts with increasing solvent polarity (Table 1). This is indicative of a small difference between the dipole moments of the ground and FC excited state.

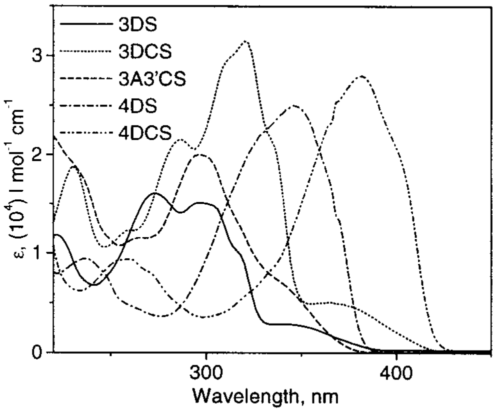

Figure 1. UV absorption spectra of 3DS, 4DS, 3A3′CS, 3DCS, and 4DCS in methylcyclohexane.

TABLE 1: Maxima of UV Absorption (λ_{Abs}) and Fluorescence (λ_{fl}), Fluorescence-Band Half-Width ($\Delta\nu_{1/2}$), Difference between the Maxima of Fluorescence at 298 and 77 K ($\Delta\lambda_{fl} = \lambda_{fl}^{298\,K} - \lambda_{fl}^{77\,K}$), Energies of the (0−0) Transition (E_s), and Stokes Shifts ($\Delta\nu_{st}$) in Methylcyclohexane (MC), 2-Methyltetrahydrofuran (MTHF), Acetonitrile (ACN), and Ethanol (EtOH) Solution

compd	solvent	λ_{abs} (nm)[a]	λ_{fl} (nm)[a]	$\Delta\nu_{1/2}$ (cm^{-1})	$\Delta\lambda_{fl}$ (nm)	E_s (eV)[a]	$\Delta\nu_{st}$ (cm^{-1})
3DS	MC	298, 342	413	3435	−2	3.27	4689
	MTHF	300, 344	444	3292	19	3.08	6547
	EtOH	300, 345	462	3811	35		7340
	ACN	298, 344	470	3668			7793
4DS[b]	MC	346	382, 401	3322	−1, −5	3.31	3326
	Et_2O	349	407	3600			4083
	EtOH	348	433	3689			5641
	ACN	351	440	3306			5763
3A3′CS	MC	298, 349[c]	402	3731	−49	3.36	3777
	MTHF	300, 354[c]	463	3320	28		6810
	EtOH	300, 350[c]	491	3866	47		8205
	ACN	298, 352[c]	483	4071			7705
3DCS	MC	320, 364	426, 443	3278	−2, −9	3.05	4378
	MTHF	320, 368	503	2699	41	2.72	7744
	EtOH	320, 368	533	3618	66		8412
	ACN	319, 368	546	3517			8859
4DCS[d]	MC	382	417, 441	2788	−4, −7	3.04	2868
	MTHF	384	491	2904	66		5675
	EtOH	385	524				6890
	ACN	383	532				7313

[a] For comparison, *trans*-stilbene: $\lambda_{abs} = 294$ nm in hexane,[55] $\lambda_{fl} = 347$ nm and $E_s = 3.80$ eV in methylpentane.[56] [b] Data from ref 14, except values in MC, $\Delta\lambda$, and E_s. [c] Shoulder. [d] Data from ref 11, except values in MC, $\Delta\lambda$, and E_s.

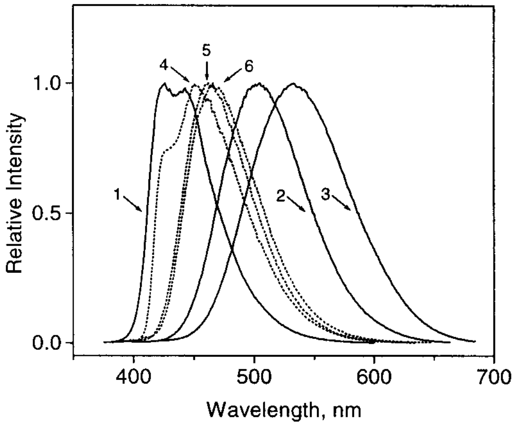

Figure 2. Fluorescence spectra of 3DCS in methylcyclohexane, 2-methyltetrahydrofuran and ethanol at 298 (1−3) and 77 K (4−6).

The 3- and 4-aminostilbenes are fluorescent in both hydroxylic and non-hydroxylic solvents. The fluorescence spectra of 3DCS in several solvents at room temperature and 77 K are shown in Figure 2. The weak vibrational structure observed in methylcyclohexane (MC), but not in more polar solvents, is similar to that of *trans*-stilbene which is attributed to vibration of the vinyl hydrogens.[29] The fluorescence spectra of 3DS and 3A3′CS are structureless in all solvents. In contrast to the absorption spectra, the maxima of the fluorescence spectra show a considerable red shift from MC to acetonitrile (ACN), 57 nm for 3DS, 81 nm for 3A3′CS, and 115 nm for 3DCS (Figure 2). The fluorescence maxima (λ_{fl}) and half-bandwidth ($\Delta\nu_{1/2}$) of the aminostilbenes are reported in Table 1 and are independent of excitation wavelength.

The 3-aminostilbenes are expected to exist as mixtures of rotamers, two in the case of 3DS or 3DCS and four in the case of 3A3′CS. The presence of multiple rotamers with different emission maxima should result in an increase in the fluorescence bandwidth. However, the values of $\Delta\nu_{1/2}$ are only slightly larger for 3DS and 3DCS when compared to the values for the

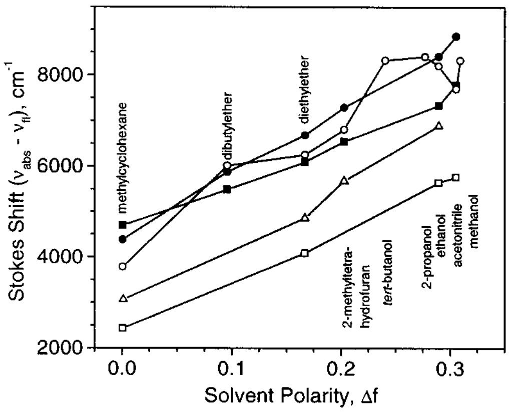

Figure 3. Solvatochromic plot of Stokes shifts for 3DS (■), 3A3′CS (○), 3DCS (●), 4DS (□), and 4DCS (△). The solvent polarity function corresponds to eq 1.

4-aminostilbenes 4DS and 4DCS (Table 1). Somewhat larger values are found for 3A3′CS which may exist as a mixture of four different rotamers. There is only a slight increase in $\Delta\nu_{1/2}$ with the solvent polarity. The energy differences between the ground state rotamers of the 3-aminostilbenes, calculated by AM1, are less than 0.1 kcal/mol and the differences between their calculated singlet energies (ZINDO)[30] are less than 0.2 kcal/mol. Whereas it is possible that a single rotamer predominates at room temperature, it is more likely that the different rotamers have essentially identical absorption and fluorescence spectra and fluorescence decay times (vide infra).

Solvatochromic Measurements and Dipole Moments. The Stokes shifts, $\Delta\nu_{st}$, of the aminostilbenes, calculated from the maxima of the absorption and fluorescence spectra, are reported in Table 1. The Stokes shifts provide a measure of the energy difference between the FC and CT states and are larger by a factor of 1.5−2 for the 3-aminostilbenes vs their 4-amino analogues. The larger values for the 3-aminostilbenes result from slightly shorter wavelengths of the absorption maxima and longer wavelengths of the fluorescence maxima. Shown in Figure 3 is a plot of the Stokes shift vs 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. The slopes in Figure 3 are mainly determined by the solvent dependence of the fluorescence maxima.

The dipole moments of the Franck−Condon (FC) excited state (μ_{FC}) and the charge transfer (CT) excited state (μ_{CT}) can be calculated from the solvatochromism of the UV absorption and the fluorescence spectra. The solvent dependence of the energies of the UV absorption and fluorescence emission can be expressed by eqs 2 and 3, respectively[31−33]

$$\nu_{abs} = -[(1/4\pi\epsilon_0)(2/hca^3)]\mu_g(\mu_e^{FC} - \mu_g)\Delta f + \text{const} \quad (2)$$

$$m_{abs} = -[(1/4\pi\epsilon_0)(2/hca^3)]\mu_g(\mu_e^{FC} - \mu_g)$$

$$\nu_{fl} = -[(1/4\pi\epsilon_0)(2/hca^3)]\mu_e^{CT}(\mu_e^{CT} - \mu_g^{FC})\Delta f + \text{const}' \quad (3)$$

$$m_{fl} = -\ [(1/4\pi\epsilon_0)(2/hca^3)]\mu_e^{CT}(\mu_e^{CT} - \mu_g)$$

where a is the solvent cavity (Onsager) radius. The ground state dipole moments, μ_g, are calculated using the INDO/S-CIS-SCF (ZINDO) algorithm.[30] The dipole moments the FC excited state, μ_{FC}, and the CT excited state, μ_{CT}, respectively, can be calculated from the slope m_{abs} given by the plot of ν_{abs} vs Δf and from the slope m_{fl} of the plot ν_{fl} vs Δf, assuming that $\mu_g^{FC} = \mu_g$. Both dipole moments are assumed to be independent of the solvent polarity. Values of the calculated dipole moments of the 3-aminostilbenes are summarized in Table 2 along with values from the literature for 4DS and 4DCS.

TABLE 2: Dipole Moments of the Ground, FC, and CT State Calculated from the Solvatochromic Data Using Eqs 1 and 2

	μ_g (D)[a]	μ_{FC} (D)[b]	μ_{CT} (D)[b]
3DS	1.7	7.1	12.1
4DS	1.8	7.7[c]	12.4[c]
3A3′CS	5.6	8.4	20.4
3DCS	6.5	10.1	21.8
4DCS	6.6	9.0[d]	21.0[d]

[a] Calculated by INDO/S-CIS-SCF (ZINDO).[53] [b] Values used for the Onsager radius: 5 Å for 3DS and 6 Å for 3A3′CS and 3D4′CS, cf. refs 21 and 25. [c] Absorption maxima for calculation of μ_{FC} and μ_{CT} from ref 14. [d] Data from ref 21.

The calculated values of μ_g for 3DS and 4DS are smaller than those for the donor−acceptor substituted aminostilbenes. This is also the case for the values of μ_{FC}. However, the difference between ground state and FC dipole moments is much larger for 3DS and 4DS than for the donor−acceptor stilbenes. The values of μ_{CT} are larger than those of μ_{FC} for all of the 3-aminostilbenes. This indicates that full CT occurs sequentially via relaxation of the FC state to the CT state, as proposed for 4DCS by Il'ichev et al.[21] The values of μ_{CT} for the *m*-aminostilbenes 3A3′CS and 3DCS are similar to that for 4DCS indicating that the location of the donor and acceptor at the meta vs para position has little effect on the observed dipole moment. This is somewhat surprising as through-resonance might have been expected to result in larger dipole moments for the 4,4′-donor−acceptor stilbenes. In addition, the similar values of μ_{CT} for 3DS vs 3AS ($\mu = 11.9$ D[25]) and for 3DCS vs 3A′CS indicate that a dimethylamino group provides little advantage over a simple amino group as the electron donor, in spite of the lower oxidation potentials of tertiary vs primary amines.[34] The room temperature fluorescence behavior of the 3-aminostilbenes is consistent with emission from a single CT state in all solvents.

Approximately linear plots of Stokes shift vs Δf are obtained for the dimethlyaminostilbenes 3DS, 4DS, 3DCS, and 4DCS in both hydroxylic (methanol and ethanol) and non-hydroxylic solvents (Figure 3). Differences in the dynamic behavior of the fluorescence of 4DCS in methanol vs ACN led to the proposal of a specific 1:1 solvent interaction with methanol; however, the CT process was concluded to dominate the Stokes shift.[20] In contrast, the Stokes shifts for 3A3′CS are larger for hydroxylic solvents than for non-hydroxylic solvents with similar or even smaller values of Δf. Similar specific solvent effects have been observed for the fluorescence spectra of other primary aminostilbenes[35,36] and for aniline[37] but not for their dimethylamino analogues.

The observation of larger Stokes shifts for the primary aminostilbenes and aniline in hydroxylic vs non-hydroxylic solvents might indicate a role for hydrogen bonding. The hydrogen bond acceptor ability of the amine lone pair would be expected to decrease upon formation of the CT excited state; however, the hydrogen bond donor ability of the amine might be expected to increase. In accord with these expectations, the deviation of the Stokes shift for 3A3′CS from the line defined by non-hydroxylic solvents follows the order *t*-butanol >

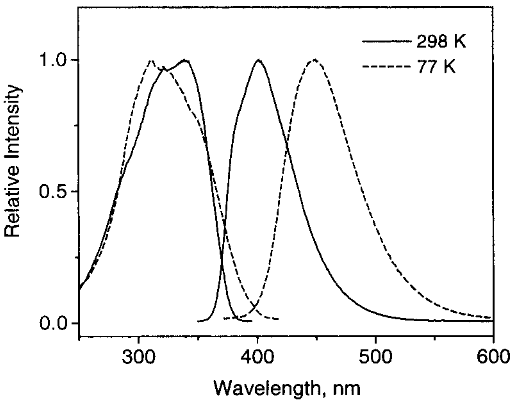

Figure 4. Fluorescence spectra of 3A3′CS in methylcyclohexane at 298 and 77 K.

i-propanol > ethanol ∼ methanol, which parallels their hydrogen bond acceptor (Taft β) abilities rather than their hydrogen bond donor abilities (Taft α).[38] Alternatively, the alcohol solvents may interact with the CT singlet states of primary aromatic amines by a Lewis acid−base interaction, the oxygen lone pair serving as donor and the electron deficient nitrogen as acceptor.[39] The order of alcohol Stokes shifts and the observation that the value for diethyl ether also lies well above the line defined by MC and ACN (Figure 3) are consistent with this explanation. The absence of similar Stokes shifts for tertiary aminostilbenes would then reflect either a more hindered or weaker nitrogen acceptor.

Low-Temperature Fluorescence Spectra. The fluorescence maximum of 3DCS in MC is slightly red-shifted at 77 K vs room temperature (Figure 2). Small red shifts are observed for the other aminostilbenes with the exception of 3A3′CS for which a large red shift (49 nm) is observed (Figure 4). Blue shifts are observed at low temperature for all of the aminostilbenes in the more polar solvents 2-methyltetrahydrofuran (MTHF), and ethanol. Values of the shift in fluorescence maximum at 77 K vs room temperature, $\Delta\lambda_{fl}$, are reported in Table 1.

The blue shifts reflect the change in solvent properties (polarity, polarizability, and viscosity) upon decreasing the temperature. For example the Δf value (eq 1) of MTHF decreases from a value of 0.203 at 298 K to 0.0293 at 77 K. The high viscosity of the 77 K glasses may also inhibit geometric relaxation in the CT state. Though the exact nature of the relaxation process from the FC to the CT state is not clear, it can be assumed that some change of the geometry, such as the rotation of single bonds or change of the bond angles, takes place that can be frozen out at low temperatures. However, jet experiments with 4DCS indicate that the conformational change upon excitation is minimal.[20]

The red shift in the fluorescence emission maximum of 3A3′CS in MC at 77 K is accompanied by a blue shift in the fluorescence excitation spectrum (Figure 4). These spectroscopic changes are similar to those reported for aggregates of *trans*-stilbene.[40−42] Thus, the 77 K spectra of 3A3′CS is tentatively assigned to aggregates or microcrystallites. Similar 77 K spectra are observed for 3-aminostilbene and 3,5-diaminostilbene but not for any of the dimethylaminostilbenes in MC.[35] The larger dimethylamino group may interfere with ground state aggregation. Alternatively, ground state hydrogen bonding of the primary amine may promote aggregation. Red-shifted fluorescence spectra were also reported for several nitrostilbenes in MTHF at low temperature but no explanation was given.[16]

Quantum Yields for Fluorescence and Photoisomerization and Singlet Lifetimes. The fluorescence quantum yields, Φ_{fl}, for the aminostilbenes in several solvents are reported in Table 3. Values of $0.5 < \Phi_{fl} < 0.7$ are observed for the 3-aminostilbenes in the nonpolar solvent MC, approximately an order of magnitude larger than the values of Φ_{fl} for the 4-aminostilbenes. The values of Φ_{fl} for the 3-aminostilbenes decrease with increasing solvent polarity, the largest decrease being observed for 3DS. In contrast, the values of Φ_{fl} for 4DS and 4DCS increase with increasing solvent polarity. The temperature dependence of the relative fluorescence intensity is shown in Figure 5. The fluorescence intensities for 3DCS in MC and for 3DS and 3A3′CS in ethanol increase slightly with decreasing temperature, plausibly due to a decrease in solvent volume. However, the quantum yield for 3A3′CS in MC decreases sharply at temperatures below 220 K (Figure 5). This decrease

TABLE 3: Quantum Yields for Fluorescence and Photoisomerization, Fluorescence Decay Times at 298 and 77 K, Rate Constants for Fluorescence Decay, Nonradiative Decay, Intersystem Crossing, and Internal Conversion in Solvents of Different Polarity

compd	solvent	Φ_{fl}	Φ_{tc}	$\tau_{fl}^{298\ K}$ (ns)	$\tau_{fl}^{77\ K}$ (ns)	k_{fl} (10^8 s^{-1})	k_{nr} (10^8 s^{-1})[a]	k_{isc} (10^8 s^{-1})[b]	k_{ic} (10^8 s^{-1})[c]
3DS	MC	0.72	0.08	13.0	13.0	0.55	0.21	0.13	
	MTHF	0.33	0.44	14.3	15.7	0.23	0.47	0.70	
	EtOH	0.18	0.39	12.4	16.9	0.14	0.66	0.56	
	ACN	0.20		13.1		0.15	0.61		
4DS[d]	*n*-hexane	0.030		0.1	1.7	2.9	97		
	Et$_{2O}$	0.029		0.1	1.7[e]	3.5	96		
	EtOH	0.035							
	ACN	0.037							
3A3′CS	MC	0.56	0.22	8.4	8.9	0.67	0.52	0.53	<0.01
	MTHF	0.24	0.24	8.8	11.9	0.27	0.86	0.43	0.31
	EtOH	0.09		8.3	13.4	0.11	1.1		
	ACN	0.18		11.1		0.16	0.74		
3DCS	MC	0.64	0.11	13.3	12.9	0.48	0.27	0.17	0.1
	MTHF	0.14	0.26	11.5	14.6	0.12	0.75	0.68	0.58
	EtOH	0.03	0.24	7.7	16.3	0.043	1.28	0.36	0.35
	ACN	0.05		13.5		0.038	0.70		
4DCS[f]	cyclohexane	0.03	0.45	0.085[g]	1.7[h]	3.53	114		
	MTHF	0.06	0.4	0.46[g]	1.7[i]	1.52	16.7		
	EtOH	0.07	0.5	0.52[g]		2.5			
	ACN	0.13	0.4						

[a] $k_{nr} = 1/\tau_{fl}(298\ K) - k_{fl}$. [b] $k_{isc} = 2\Phi_{tc}/\tau_{fl}$. [c] $k_{ic} = 1/\tau_{fl}(298\ K) - k_{fl} - k_{isc}$, no k_{ic} values are given in ethanol due to H-bonding interactions that contribute to the nonradiative decay. [d] Data from ref 14. [e] Lifetime maximum: 1.9 ns at 200 K. [f] Data from ref 11. [g] Data from ref 19. [h] Data from ref 56 in *n*-hexane. [i] Data from ref 13, lifetime maximum: 2.2 ns at 180 K in ethanol.

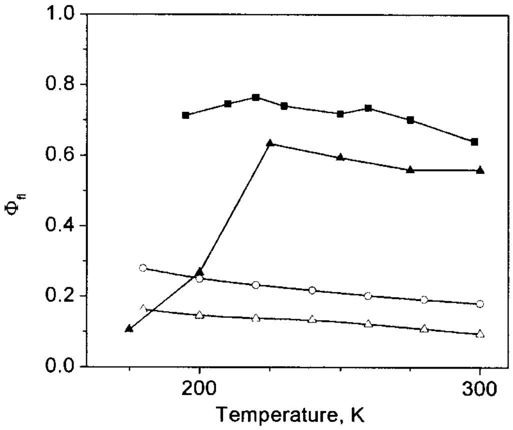

Figure 5. Temperature dependence of the fluorescence quantum yields for 3DCS (■) and 3A3′CS (▲) in methylcyclohexane and 3DS (○) and 3A3′CS (△) in ethanol.

is assigned to aggregation, in accord with the spectral shifts (Figure 4) described above.

The fluorescence lifetimes of the aminostilbenes in several solvents at room temperature are also reported in Table 3. All decays are best fit by single-exponential functions. The lifetimes of the 3-aminostilbenes are about 1 order of magnitude longer in comparison to the analogous para derivatives 4DS and 4DCS, in accord with their higher fluorescence quantum yields. The lifetimes of the 3-aminostilbenes display only small variation with solvent polarity, the largest change being observed for 3DCS in ethanol vs non-hydroxylic solvents. In contrast, the lifetime of 4DCS increases ca. 6-fold in ACN vs MC.

The fluorescence rate constants ($k_{fl} = \Phi_{fl}/\tau_{fl}$) and the overall nonradiative deactivation ($k_{nr} = 1/\tau_{fl}^{298\,K} - k_{fl}$) can be calculated from the fluorescence quantum yields and lifetimes (Table 3). Values of k_{fl} for the 3-aminostilbenes are lower than those for their para analogues as a consequence of the lower oscillator strength of their lowest $\pi-\pi^*$ transitions (Figure 1).[25] Values of k_{nr} are also lower for the 3- vs 4-aminostilbenes. The long singlet lifetimes of the 3-aminostilbenes are thus a consequence of their relatively small values of both k_{fl} and k_{nr}. Values of k_{fl} for the 3-aminostilbenes decrease with increasing solvent polarity, whereas the values of k_{nr} are generally larger in ACN vs MC. These changes account for the decrease in Φ_{fl} with increasing solvent polarity.

The singlet lifetimes of the 3-aminostilbenes have been measured as a function of temperature between 77 and 298 K in MC and ethanol solution. The lifetimes in fluid MC are independent of temperature, but decrease slightly near the glass transition temperature of the solvent (ca. 120 K). Similar behavior has been reported for *trans*-3-aminostilbene (3AS).[25] In contrast, the singlet lifetimes of the *m*-aminostilbenes in ethanol solution gradually increase with decreasing temperature over the entire range from 300 to 80 K, as shown in Figure 6 for 3DCS.

Quantum yields for photoisomerization of the aminostilbenes in several solvents are summarized in Table 3. Value of Φ_{tc} for the 3-aminostilbenes are generally smaller than the values of $\Phi_{tc} \sim 0.5$ reported for *trans*-stilbene or 4DCS. The low values of Φ_{tc} are consistent with the large values of Φ_{fl} for the 3-aminostilbenes. The values of Φ_{tc} for 3DS and 3DCS increases with increasing solvent polarity, as previously observed for 3AS.[25] Values for 3A3′CS and display only modest solvent dependence as is the case for *trans*-stilbene and 4DCS.

Nonradiative Decay in Nonpolar Solvent. A generalized scheme for the photochemical behavior of the aminostilbenes is shown in Figure 7. The CT singlet state can decay via activated twisting about the double bond or via fluorescence, intersystem crossing, and internal conversion, which are normally assumed to be unactivated processes (eq 4).

$$1/\tau_{fl} = k_{fl} + k_{isc} + k_{ic} + A_0 e^{(-E_a/RT)} \qquad (4)$$

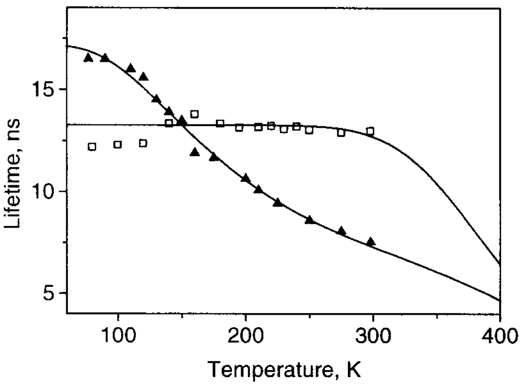

Figure 6. Temperature dependence of the lifetimes of 3DS in methylcyclohexane (□) and 3DCS in ethanol (▲). The lines represent the fits through the data points of 3DS and 3DCS obtained using eq 4.

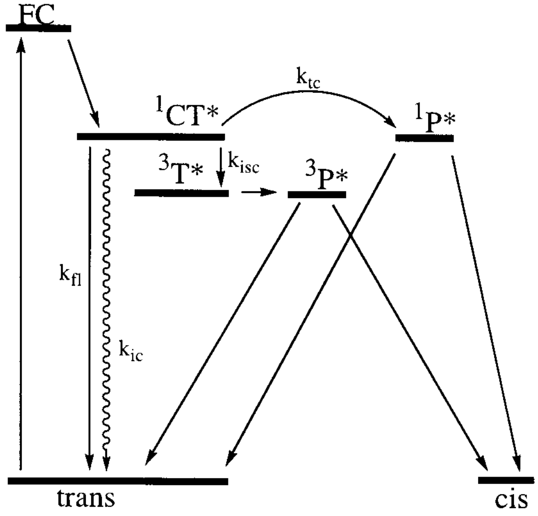

Figure 7. Simplified scheme for the formation and decay of the fluorescent ^{1}CT* state of the aminostilbenes.

The fluorescence lifetime data for temperatures higher than 140 K indicate that there is no activated process that competes with fluorescence decay in fluid solution. The lifetime data for 3DS, 3A3′CS, and 3DCS in MC can be fit to eq 4 with values of E_a > 7 kcal/mol and $A_0 = 10^{12}$ s^{-1} using the experimental value for k_{fl} (Figure 6).

The large barrier for singlet state torsion of the 3-aminostilbenes is similar to that previously observed for 3-aminostilbene (3AS).[25] In the case of 3AS we suggested that the barrier resulted from stabilization of the planar singlet ^{1}S* but not the twisted singlet ^{1}P* by the *m*-amino substituent. The energies of the ^{1}S* states can be determined from their electronic spectra and are similar for stilbenes with the same substituents in the meta vs para positions. The energies of the ^{1}P* states cannot be determined experimentally. However, ^{1}P* is predicted to have either biradical or zwitterionic character, depending upon the substituents.[43,44] In either case, a *m*-amino substituent should be less effective in stabilizing ^{1}P* than a para substituent due to the absence of direct conjugation with the benzylic radical or cation, resulting in a larger activation energy for torsion of the meta- vs *p*-aminostilbenes (Figure 7). The observation of large torsional barriers for 3A3′CS and 3DCS establishes that the meta amino effect operates for donor−acceptor stilbenes as well other 3-aminostilbenes.[24,25]

The similar singlet lifetimes for 3A3′CS and 3DCS in MC and ACN solution indicate that the tosional barrier remains high in the polar solvent. The barrier for *trans*-stilbene decreases slightly with increasing solvent polarity, from 3.5 kcal/mol in hexane to 2.4 kcal/mol in ACN.[5,6] However, the barrier for 4DCS increases with increasing solvent polarity from 3.3 kcal/mol in heptane to 5.4 kcal/mol in ACN.[21] This difference can be related to the polar character of the $^1S^*$ and $^1P^*$ states. In the case of stilbene, $^1S^*$ is nonpolar and $^1P^*$ is zwitterionic in character, whereas in the case of 4DCS the $^1S^*$ ($^1CT^*$) state is highly polar and the $^1P^*$ biradicaloid.[11,18,19,44,45] Thus increasing the solvent polarity results in more exergonic torsion for *trans*-stilbene but less exergonic torsion for 4DCS. The nonradiative rate constant for 4DS is independent of the solvent polarity (Table 3),[14] suggesting that the polarities of the $^1S^*$ and $^1P^*$ states are similar.

The relatively high barrier for singlet state double bond twisting and the low fluorescence rate constant permit other nonradiative decay pathways to compete with the fluorescence decay in case of the 3-aminostilbenes. Photoisomerization is presumed to occur via intersystem crossing to the planar triplet $^3T^*$ followed by torsion on the triplet state surface to the perpendicular triplet $^3P^*$ (Figure 7). Efficient intersystem crossing has also been observed for 4-nitro, 4-acetyl, and 4-bromostilbene.[7−9] In each of these cases, the rate constant for intersystem crossing is faster than that for *trans*-stilbene as a consequence of increased spin−orbit coupling. This results from the presence of lowest singlet n,π^* singlet states for the nitro and acetyl substituents and a heavy atom effect for the bromo substituent. The triplet state $^3T^*$, populated by triplet sensitization of *trans*-stilbene or by intersystem crossing in case of nitrostilbenes, undergoes barrierless torsion to the $^3P^*$ state. A fast equilibrium between $^3T^*$ and $^3P^*$ has been suggested.[1,3] In contrast, twisting of the triplet state of 4-bromostilbene is reported to be an activated process.[45]

The rate constants for intersystem crossing of the 3-aminostilbenes can be calculated from the experimental values of Φ_{tc} and τ_{fl}, assuming that the perpendicular $^3P^*$ state decays in a 1:1 ratio to the cis and trans isomers ($\Phi_{isc} \sim 2\Phi_{tc}$). The calculated values k_{isc} of $(1-7) \times 10^7$ s^{-1} (Table 3) are similar to the estimated values of 3.9×10^7 s^{-1} for *trans*-stilbene and 2.4×10^7 s^{-1} for 3AS in ACN solution.[3,25] The values of k_{isc} for the 3-aminostilbenes increase modestly with increasing solvent polarity. This may result from a decrease in the energy gap between the relatively polar $^1CT^*$ state and nonpolar $^3T^*$ state with increasing solvent polarity.[46] This increase in k_{isc} is responsible, in part, for the decrease in Φ_{fl} with increasing solvent polarity. The S_1-T_1 energy gap of 4,4′-donor−acceptor substituted *trans*-stilbenes also decreases with increasing acceptor strength; however, intersystem crossing has been found to be negligible in comparison to the other singlet state deactivation pathways.[47]

The sum of the fluorescence and intersystem crossing quantum yields for the 3-aminostilbenes in MC is ≥0.85. Thus, other nonradiative decay pathways for the singlet state are of relatively minor importance. This is also the case for 3DS in polar solvents. However, the sum $\Phi_{fl} + \Phi_{isc}$ for 3A3′CS and 3DCS is significantly smaller than unity in more polar solvents. This raises the question of the nature of the nonradiative decay pathway(s) in these solvents. A possible answer is provided by the temperature dependence of the singlet lifetimes in ethanol solution.

TABLE 4: Activation Parameters (A_0, E_a) from Fitting of the Temperature Dependence of the Lifetimes in Ethanol to Eq 4

	$k_{isc} + k_{ic}$ (10^8 s^{-1})	A_0 (10^8 s^{-1})	E_a[a] (kcal/mol)
3DS	0.41	2.3	0.91(0.85)
3A3′CS	0.65	8.5	1.7(1.6)
3DCS	0.54	3.6	0.91(0.99)

[a] Values in parentheses are obtained from the slopes of Arrhenius plots.

Nonradiative Decay in Polar Solvents. The singlet lifetimes of 3DS, 3A3′CS, and 3DCS in ethanol solution increase with decreasing temperature, as shown for 3DCS in Figure 6. Fitting of these data to eq 4 using the measured values of k_{fl} (Table 3) provides values of $A_0 \sim 10^8$ s^{-1} and $E_a \sim 1-2$ kcal/mol for the activated decay process and values of $(k_{isc} + k_{ic}) \sim 5 \times 10^8$ s^{-1}(Table 4). Typical A_0 values for singlet state isomerization are reported to be $10^{12}-10^{14}$ s^{-1},[1] much higher than the values in Table 4. In addition, the values of E_a in Table 4 are much smaller than those for MC solution (>7 kcal/mol), even though the room temperature decay times of the 3-aminostilbenes are similar in MC and ethanol. This would appear to rule out singlet state isomerization as the low preexponential, low activation energy decay pathway, leaving weakly activated intersystem crossing and internal conversion as the candidates.

Thermally activated intersystem crossing has been observed for some anthracene derivatives in which the second triplet state is slightly higher in energy that the lowest singlet.[48] Goerner has proposed that intersystem crossing to the second triplet also occurs in the case of 4-halogenated stilbenes.[45] It is possible that a decrease in the S−T energy gap with increasing solvent polarity could open an activated decay channel that is not observed in nonpolar solvents. However, since $\Phi_{fl} + 2\Phi_{tc} < 1$ for 3A3′CS and 3DCS in ethanol, this explanation would require that the triplet state, once formed, decays with a trans:cis isomer ratio >1:1. Thus, both the intersystem crossing and triplet decay processes would need to be solvent dependent. The alternative is weakly activated internal conversion. Rate constants for internal conversion of aromatic hydrocarbons obey the rate law given in eq 5

$$k_{ic} = 10^{13}e^{-\alpha E_s} \qquad (5)$$

where E_s is the singlet energy and the constant $\alpha = 4.85$.[48] Values of k_{ic} for 3A3′CS and 3DCS calculated from the measured singlet lifetime and quantum yield data ($\Phi_{ic} = 1 - (\Phi_{fl} + 2\Phi_{tc})$) are reported in the final column of Table 3. The calculated values for MC solution are similar to those obtained from eq 5 and the measured singlet energies. The calculated values of k_{ic} increase with increasing solvent polarity, as expected, based on the decrease in singlet energy with increasing solvent polarity (Table 1).

Internal conversion has been suggested as a decay channel that accounts up to 90% of $^1S^*$ decay for several aminonitrostilbenes.[16] In this case, internal conversion is proposed to occur via a singlet state (A*) which is assumed to be more polar than the $^1S^*$ state and is associated with internal electron transfer. The agreement between the experimental and calculated values of k_{ic} for the 3-aminostilbenes indicates that there is no need to propose the involvement of a singlet state other than $^1CT^*$ (Figure 7).

Conclusions

This study extends the scope of the "*meta*-amino effect" as previously observed for *trans*-3-aminostilbene[24,25] to tertiary 3-aminostilbenes and donor−acceptor substituted stilbenes. The meta effect, as applied to *trans*-aminostilbenes, represents high fluorescence quantum yields and long singlet lifetimes, which are a consequence of a high barrier for double bond torsion on the excited singlet surface, and a low rate constant for fluorescence decay. Analysis of their solvatochromic behavior indicates that the charge separation processes for both the 3- and 4-aminostilbenes occur in two steps, formation of the FC singlet followed by relaxation to the CT singlet. The high fluorescence quantum yields and large dipole moments of the ^{1}CT* states of 3A3′CS and 3DCS make them potentially attractive as solvatochromic probe molecules.

As a consequence of the long singlet lifetimes for the 3-aminostilbenes, nonradiative decay processes which are not observed for *trans*-stilbene or the 4-aminostilbenes can compete with fluorescence. Intersystem crossing followed by decay of the triplet to trans and cis ground states provides the only pathway for photoisomerization of the 3-aminostilbenes and the predominant nonradiative decay pathway in nonpolar solvents. In polar solvents, a second, weakly activated, nonradiative pathway is observed for 3A3′CS and 3DCS. This pathway is tentatively assigned to singlet state internal conversion on the basis of its singlet-energy dependence.

The primary aminostilbene 3A3′CS, but not its tertiary analogues, displays larger solvent-induced fluorescence shifts in alcohol vs non-hydroxylic solvents. These shifts may reflect either excited state hydrogen bonding in which the amine serves as the donor and the alcohol as acceptor or a Lewis acid−base interaction in which the electron-deficient amine serves as the acceptor and the alcohol as a lone-pair donor. Another respect in which 3A3′CS differs from its tertiary analogues is the observation of a decrease in fluorescence intensity, red-shifted emission, and blue-shifted fluorescence excitation at low temperature in methylcyclohexane. Aggregation of the primary amine can account for these observations.

Experimental Section

Materials. The 3-nitrostilbenes were synthesized by Wittig reaction[49] from 3-nitrobenzaldehyde and the corresponding triphenylphosphonium chloride in a methylene dichloride/water (50% in K_2CO_3) system with tetrabutylammonium iodide as phase-transfer catalyst (10 mol %). The trans isomer was enriched by refluxing the mixture of the isomers in benzene using catalytic amounts of iodine. 3DS and 3DCS were obtained from the 3-nitrostilbenes by reduction of the nitro to the amino group by using Zn/HCl−CH_3COOH as the reduction agent[50] and subsequent methylation to the dimethylaminostilbenes by reaction with formaldehyde and cyanoborohydride.[51] The compounds were purified by gravity column chromatography on silica gel (230−400mesh, hexanes−EtOAc (90:10)). The purity of *trans*-3DS, *trans*-3A3′CS, and *trans*-3DCS was estimated to be >98.5% by using GC. Their identity was checked by ^{1}H NMR. Methylcyclohexane, dibutyl ether, diethyl ether, ethanol, and ACN (all Aldrich spectro grade) were used as received. 2-Methyltetrahydrofuran (Aldrich) was distilled from Na prior to use.

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)[52] was used as standard for the fluorescence quantum yield determinations with solvent refractive index correction and the optical density of all solutions was about 0.1 at the wavelength of excitation. All fluorescence spectra are uncorrected, and an error of $\pm$10% is estimated for the fluorescence quantum yields. Fluorescence decays were measured on a single photon counting setup described in detail elsewhere.[25] Quantum yields of photoisomerization were measured at 313 nm using an optical bench equipped with a 200 W Hg (Xe) high-pressure lamp and a monochromator. The optical density of the solutions was >2. *trans*-Stilbene was used as standard ($\Phi_{iso} = 0.5$ in methylcyclohexane).[1] The extent of photoisomerization (<10%) was recorded by using a HPLC (HP1090, Chromeleon 6.00 (Dionex), Hypersil silica 5 μm, hexane:EtOAc (90:10)). 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.[53,54] The structures used in the ZINDO calculations were based on ground state, SCF/AM1, optimized geometries using MOPAC (version 94.10).[54]

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