

The Excited State Behavior of Aminostilbenes. A New Example of the Meta Effect

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The enhanced photochemical reactivity of meta- vs para-substituted benzenoid compounds was first described by Havinga.¹ The “meta effect” was rationalized by Zimmerman² resulting from selective transmission of electron donation or withdrawal on the basis of simple Hückel theory. We report here a new example of the meta effect: namely, the marked difference in excited state behavior of the trans isomers of *m*- vs *p*-aminostilbenes **1**–**3** (Chart 1).³ In comparison to the para derivatives, the singlet states of the meta derivatives have greater charge transfer character, significantly longer lifetimes, and higher fluorescence quantum yields. Moreover, the meta but not the para isomers are subject to quenching by methanol, and in one case, regioselective addition of methanol to a singlet stilbene is observed.

The spectroscopy and photochemistry of donor–acceptor-substituted stilbenes such as 4-(dimethylamino)-4'-cyanostilbene (DCS) have been extensively investigated.^{4–6} The pronounced solvent dependence of the fluorescence behavior of such molecules has been attributed to rapid relaxation of the initially formed Franck–Condon excited state to a charge-transfer (CT) state. Trans → cis isomerization also originates from the CT state via twisting about the central double bond to form the perpendicular excited species which decays to a mixture of cis and trans isomers.^{6,7} The singlet state behavior of 4-amino-4'-(methoxycarbonyl)stilbene (**1p**) is similar to that of DCS. The absorption spectrum of **1p** (Figure 1) is red-shifted with respect to that of stilbene ($\lambda_{\text{max}} = 295$ nm). Increasing solvent polarity results in a small red shift in the absorption maximum but a substantial red shift in the fluorescence maximum (Table 1) and a loss of the vibrational structure observed in nonpolar solvents.⁸ A dipole moment of 14.4 D can be estimated for the CT state of **1p** using the Lippert–Mataga equation⁹ and a solvent cavity radius of 5 Å. As for DCS, the singlet lifetime of the CT state of **1p** is short in nonpolar solvents and increases modestly in more polar solvents, as do the fluorescence and photoisomerization quantum yields (Table 1).

The behavior of the meta isomer **1m** differs from that of **1p** in several respects: (a) The lowest energy absorption maximum of **1m** is at shorter wavelength and has a lower oscillator strength

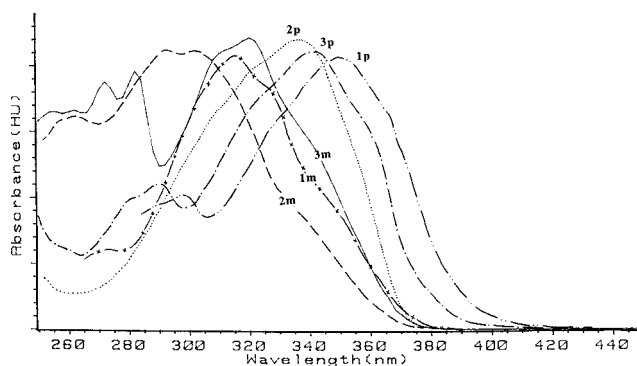


Figure 1. The absorption spectra of aminostilbenes **1p** (---), **1m** (-x-), **2p** (···), **2m** (- - -), **3p** (---), and **3m** (—) in cyclohexane solution.

Chart 1

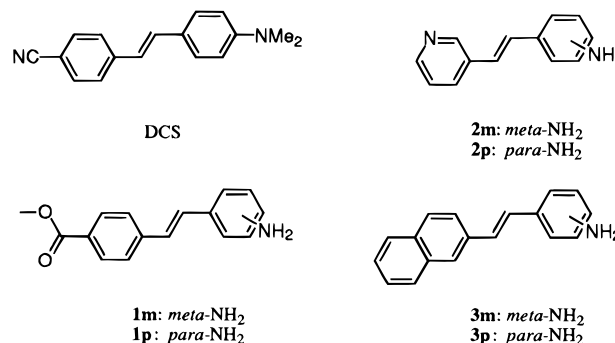


Table 1. Fluorescence Emission Data and Quantum Yields for Trans → Cis Photoisomerization ($\Phi_{E,Z}$) for Aminostilbenes **1**–**3** in Nonpolar and Polar Solvents

	sol-vent	1m	1p	2m	2p	3m	3p
$\lambda_{\text{max,flu}}$ (nm)	cHex	407	412	394	390	393	392
	MeCN	521	501	467	446	459	451
$\mu_{\text{e}}(\text{D})^b$		14.9	14.4	13.2	12.1	12.4	11.8
Φ_{F}^c	cHex	0.61	0.024	0.76	0.023	0.78	0.084
	MeCN	0.12	0.062	0.29	0.027	0.43	0.051
τ_{F} (ns)	cHex	6.15	0.22	5.51 (31)	0.22	4.09 (46)	0.20
	(preexp %)			8.58 (69)		5.49 (54)	
$\Phi_{E,Z}^d$	MeCN	6.20	0.32	7.33 (17)	0.18	9.86 (21)	0.23
	MeOH	<i>a</i>	0.41	11.7 (83)	0.27	12.5 (79)	0.28
$\Phi_{E,Z}^d$	PhH	0.036	0.19	1.01 (99)	0.31	8.16 (57)	0.17
	MeCN	0.036	0.23	5.89 (1)	0.38	11.3 (43)	0.12

^a Fluorescence almost completely quenched. ^b Calculated according to $\nu_{\text{flu}} = -2\mu_{\text{e}}^2/hca^3\{(\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(4n^2 + 2)\}$ + constant with the assumption of solvent cavity of $a = 5$ Å. ^c Phenanthrene ($\Phi_{\text{F}} = 0.14$) as the actinometer for all compounds excited at 294 nm.²¹ ^d Light source is 313 nm.

(Figure 1).¹⁰ (b) The fluorescence maxima of **1m** are comparable to those of **1p** in nonpolar solvents and display larger solvent-induced shifts. Thus, the calculated excited state dipole moment of **1m** is larger than that of **1p** (Table 1). No vibrational structure is observed for the fluorescence of **1m** even in cyclohexane solution or low-temperature glasses. (c) Both the singlet lifetime and fluorescence quantum yield for **1m** in cyclohexane solution are 30-fold larger than the values for **1p**. The fluorescence lifetime of **1m** is somewhat longer in benzene or diethyl ether than in cyclohexane or acetonitrile solution. The

(10) (a) Semiempirical INDO/S-SCF-CI (ZINDO) calculations^{10b} for **2m** and **2p** indicate that both isomers have lowest energy HOMO → LUMO, $\pi \rightarrow \pi^*$ transitions with similar energies (334 and 340 nm for **2m** and **2p**, respectively). However, this transition is calculated to have more extensive configuration interaction and a lower oscillator strength for **2m** vs those of **2p**. (b) Bacon, A. D.; Zerner, M. C. *Theor. Chim. Acta* **1970**, *53*, 21.

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(3) (a) The amino-substituted stilbenes **1**–**3** were synthesized by reduction of the corresponding nitrostilbenes,^{3b} which were made by Wittig reactions using the procedures of Lee and Marvel.^{3c} (b) Bellamy, F. D.; Ou, K. *Tetrahedron Lett.* **1984**, 839. (c) Lee, B. H.; Marvel, C. S. *J. Polym. Sci. Chem. Ed.* **1982**, *20*, 393.

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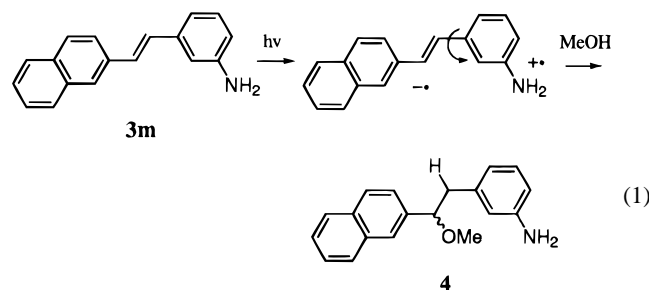
(7) Lapouyade and Rettig⁵ have proposed the involvement of a relaxed locally excited state in addition to the CT and P* (“three state” model). The “two state” model of Görner⁴ and Zachariasse⁶ is sufficient to explain our results.

(8) Fluorescence spectra are provided as Supporting Information.

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fluorescence quantum yield decreases with increasing solvent polarity, and no fluorescence is detected in methanol solution. (d) The photoisomerization quantum yield for **1m** is much smaller than that for **1p** in both benzene and acetonitrile solution.

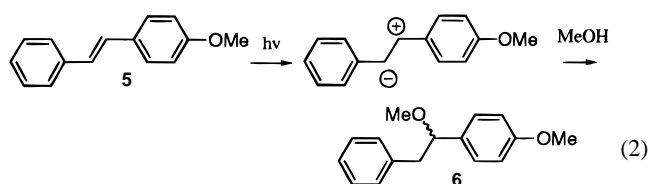
Similar differences in photochemical behavior are observed for the meta vs para isomers of *m*-(aminostyryl)pyridine (**2**) and 2-(aminostyryl)naphthalene (**3**). The absorption maxima of **2m** and **3m** are at shorter wavelength than those of their para isomers (Figure 1); however, their fluorescence maxima are at longer wavelength and display larger solvent-induced shifts in polar solvents. Compared to their para isomers, **2m** and **3m** have significantly longer decay times, larger fluorescence quantum yields, and smaller photoisomerization quantum yields. The dual exponential decay observed for **2m** and **3m** is attributed to the decay of two conformers which may differ in either aryl vinyl or anilino vinyl conformation. The absence of excitation wavelength dependence of the emission spectra indicates that the two conformer have similar spectra. Emission from a single conformer or two conformers with similar decay times could account for the observation of single exponential decay from **1m**. Dual exponential fluorescence decay might also be expected for **2p** and **3p**; however, a decay component comparable to or shorter than those reported in Table 1 would not be resolved by our lifetime apparatus. The fluorescence decay times of **2m** and **3m** are shorter in methanol than in acetonitrile, but their fluorescence is not completely quenched as it is for **1m**. Upon irradiation in methanol (or methanol-*d*₄) solution, **3m** is regioselectively converted to the solvent adduct **4** in >80% yield (eq 1).¹¹ The assignment of structure **4** is based upon mass spectral and ¹H NMR data. Methanol adduct formation is not observed for **2m**, **3m**, or any of the para isomers.



The behavior of the para isomers of **1–3** is similar to that of DCS. The smaller dipole moment of **1p** (and of **2p** or **3p**) vs DCS (21 D⁶) is consistent with its weaker donor (NH₂ vs NMe₂) and acceptor (CO₂Me vs CN) substituents. The lifetimes of all three para isomers are short (<0.4 ns), their fluorescence quantum yields are small (<0.08), and their isomerization quantum yields are moderate to large (>0.17) both in nonpolar and polar solvents. The parent stilbene and styrylpyridine also have short lifetimes, whereas the parent 2-styrylnaphthalene has a longer lifetime (5.2 and 27.6 ns for the two conformers¹²). Thus, the behavior of **3p** resembles that of the donor–acceptor stilbenes rather than that of its parent.

A clue to the possible origin of the unusual behavior of the meta isomers of **1–3** is provided by the regioselectivity of methanol addition to **3m** (eq 1). Woning et al.¹³ observed that irradiation of *p*-methoxystilbene **5** in methanol results in

formation of the adduct **6** (eq 2). Their result is consistent with



nucleophilic addition of methanol to a polarized or zwitterionic singlet state in which the positive charge is stabilized by the *p*-methoxy substituent. The formation of **4** from **3m** can be rationalized by attack of methanol on a CT state in which the positive charge is localized on the aniline ring and the negative charge on the vinyl naphthalene (eq 1). Methanol addition to styrene anion radicals is known to occur via protonation of the β carbon followed by nucleophilic capture of the resulting benzylic cation.¹⁴ The efficient quenching of **1m** and **2m** in methanol and the absence of adduct formation may result from protonation of the ester carbonyl or pyridyl lone pair, both of which should be highly basic in the CT excited state.¹⁵

A model which might explain the pronounced difference in behavior between the meta and para isomers of **1–3** is that the CT states of the meta isomers are twisted and those of the para isomers are planar.¹⁶ Twisting about the anilino–styrene bond would result in localization of the positive charge on aniline and the negative charge on styrene, in accord with the observed regiochemistry of methanol addition to **3m**. More extensive twisting for the meta vs para isomers could account for the larger singlet state dipole moments meta isomers and the observation methanol quenching of the meta but not the para isomers. It could also result in a larger barrier for twisting about the central bond which in turn could account for the significantly longer singlet lifetimes, higher fluorescence quantum yields, and lower isomerization quantum yields for the meta isomers. Further studies designed to test this model are in progress.

The *p*-dimethylamino substituent has been widely used as the electron-donor in donor–acceptor-substituted π -conjugated systems which are of interest due to their applications as nonlinear optical materials,¹⁷ laser dyes,¹⁸ fluorescence probes,¹⁹ and fluorescence brighteners.²⁰ Our results suggest that long fluorescence lifetimes and high fluorescence quantum yields may be a general characteristic of *m*-amino-substituted *trans*-1,2-diarylolefins. Preliminary results indicate that a *m*-amino effect is also observed for *cis*-1,2-diarylolefins. As such, the *m*-amino effect may prove of value in the design of new fluorescent materials.

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Supporting Information Available: An expanded version of Table 1 with data for additional solvents, the fluorescence spectra of **3m** and **3p** showing the typical solvent-dependent fluorescence behavior of both *m*- and *p*-aminostilbenes, and the fluorescence spectra of **2m** in cyclohexane showing the absence of excitation wavelength-independent fluorescence behavior (3 pages). See any current masthead page for ordering and Internet access instructions.

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(11) The formation of compound **4** was confirmed by ¹H NMR and MS: ¹H NMR (CDCl₃) δ 7.78–7.84 (m, 3H), 7.66 (s, 1H), 7.42–7.49 (m, 3H), 7.36 (s, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.49–6.56 (m, 2H), 4.48 (dd, *J* = 5.8 and 7.6 Hz), 3.21 (s, 3H), 3.60 (bs, 2H), 3.11 (dd, *J* = 7.6 and 13.9 Hz, 1H), 2.89 (dd, *J* = 5.7 and 13.8 Hz, 1H); MS (*m/e*) 277 (M⁺, 5), 171 (M⁺ – C₆H₄(NH₂)(CH₂), 100). The corresponding ¹H NMR and MS data for the compound formed from irradiation of **3m** in CD₃OD conform to the structure of deuterated **4**.

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