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The Photochemistry of *cis-ortho-*, *meta-*, and *para-*Aminostilbenes

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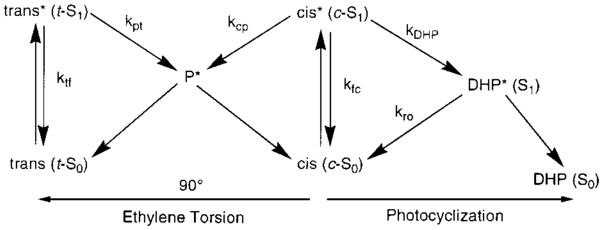
The photochemical behavior of the three isomers of *cis*-aminostilbene is reported here and compared to that of *cis*-stilbene as well as the corresponding *trans*-aminostilbenes. The absorption spectra of *cis*-, *ortho*-, and *meta*-aminostilbene are characterized by multiple low oscillator strength bands as a result of symmetry-induced configuration interaction. Fluorescence is observed for *cis-meta*-aminostilbene but not for the other two isomers, even at 77 K. The fluorescence spectrum of *cis-meta*-aminostilbene at 77 K is broad and red shifted relative to that of the trans isomer with a large Stokes shift, and its singlet lifetime in methyltetrahydrofuran at 77 K is 17.4 ns. The photocyclization quantum yield for *cis-meta*-aminostilbene in cyclohexane solution is the largest measured for a monosubstituted *cis*-stilbene and the photoisomerization quantum yield is unusually low. In contrast, the photochemical behavior of the ortho and para isomers is similar to that of most substituted *cis*-stilbenes and is dominated by photoisomerization. The excited-state potential energy surface for *cis-meta*-aminostilbene is proposed to be perturbed, as in the case of *trans-meta*-aminostilbene, resulting in striking differences in the photochemical behavior of the three positional isomers. The photochemical behavior of the ortho and para isomers is dominated at low temperatures by a nonradiative channel that has been observed for other substituted *cis*-stilbenes.

Introduction

The photochemical behavior of *trans*- (***t*-1**) and *cis*-stilbene (***c*-1**) is well-known (Scheme 1).[1−3] Whereas the excited state of *trans*-stilbene has a lifetime of 0.070 ns in nonpolar solvents,[4] the behavior of *cis*-stilbene is characterized by ultrafast events that occur on a femtosecond time scale.[5] The only unimolecular photochemical reaction for *trans*-stilbene is double bond torsion to yield a perpendicular intermediate P*, occurring via the excited singlet state as an activated process that has a barrier of 3.5 kcal/mol.[1] The behavior of the excited state of *cis*-stilbene is more complex. On the basis of time-resolved absorption and fluorescence spectroscopy, the lifetime of excited *cis*-stilbene is about 1 ps.[6,7] The short lifetime of *cis*-stilbene results from low barriers for two singlet state photoisomerization processes.[3,5] About 70% of the excited state of *cis*-stilbene decays via torsion to form P* and the remainder forms an intermediate DHP* that leads to either the formation of dihydrophenanthrene or ground state *cis*-stilbene (Scheme 1).[3,5] Due to the presence of these extremely fast deactivation channels in *cis*-stilbene, the fluorescence quantum yield (ϕ_f) is approximately 1×10^{-4}.[3] Most substituted *cis*-stilbenes studied to date have shown similar behavior; that is, they are either weakly fluorescent or nonfluorescent at room temperature and undergo cis−trans photoisomerization or form substituted dihydrophenanthrenes.[8,9]

The absorption spectra of *cis*-stilbene and most substituted *cis*-stilbenes are broad and have reduced oscillator strength relative to the trans analogues due to a nonplanar molecular geometry.[10] The low-temperature fluorescence spectra of a few substituted *cis*-stilbenes have also been studied and are broad and structureless in comparison to their trans analogues.[10−12] The Stokes shift for substituted *cis*-stilbenes is generally larger than that for the corresponding *trans*-stilbenes suggesting that a change in geometry, presumably torsional motion about the phenyl−ethenyl bond, occurs prior to emission.[11,13] The large Stokes shift observed for *cis*-stilbenes persists at 77 K, indicative of only small amplitude nuclear motion prior to emission.[11,13]

SCHEME 1



We recently reported that the photophysical behavior of trans-*ortho*- (***t*-2**), *meta*-, (***t*-3**) and *para*-aminostilbene (***t*-4**) is highly dependent upon the position of the amino substituent.[14,15] The ortho and meta substituted stilbenes, ***t*-2** and ***t*-3**, are highly fluorescent when compared with the para analogue, ***t*-4**, or all other known monosubstituted stilbenes.[16] The high fluorescence quantum yields and long singlet lifetimes were found to be due to the presence of a large barrier (≥7 kcal/mol) for singlet excited-state photoisomerization. It was also noted that the absorption spectra of ***t*-2** and ***t*-3** differed substantially from those of ***t*-4** and other para monosubstituted stilbenes.[15,17] The absorption spectrum of ***t*-4** displays a single intense long wavelength band, whereas the spectra of ***t*-2** and ***t*-3** display multiple bands of reduced oscillator strength. The spectral complexity was found to be due to local symmetry-induced configuration interaction between several singly excited $\pi \rightarrow \pi^*$ configurations resulting in the loss of oscillator strength and lowering of the energy of the S_1 state.[15]

We report here an investigation of the *cis*-aminostilbenes (***c*-2**, ***c*-3**, and ***c*-4**). The absorption spectra of the *cis*-aminostilbenes display spectral patterns similar to those of the corresponding

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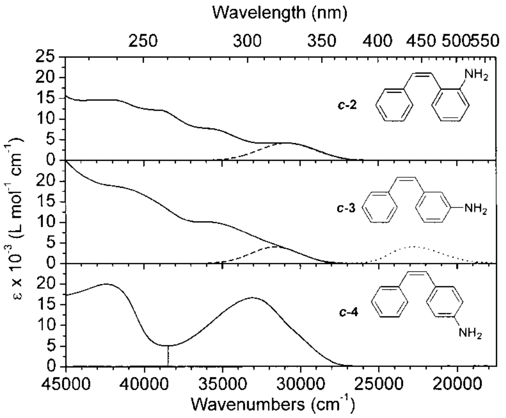


Figure 1. Absorption (solid lines) and emission (dotted) spectra for the aminostilbenes in cyclohexane. Deconvoluted Gaussian peaks are shown as dashed lines.

trans isomers. The photochemical behavior of ***c*-3** is substantially different from that ***c*-4**, as is the case for the trans isomers. However, the behavior of ***c*-2** resembles that of the para rather than the meta isomer. The origin of this behavior is explained on the basis of two competing photoisomerization reactions for ***c*-1** and the model determined for the corresponding *trans*-aminostilbene compounds.

Results and Discussion

Absorption Spectroscopy. The structures and absorption spectra of ***c*-2**, ***c*-3**, and ***c*-4** in cyclohexane solutions are shown in Figure 1. The spectra of the *cis*-aminostilbenes have similar band shape to those previously reported for the corresponding *trans*-aminostilbenes, except that they have lower molar absorptivity and are slightly blue shifted (Table 1 and Figure 1).[15] Such behavior is typical for substituted *cis*-stilbenes.[10,17] The absorption spectrum of ***c*-4** consists of a single broad band that is blue shifted relative to ***t*-4** ($\lambda_{max} = 316$ nm). The absorption spectra of ***c*-2** and ***c*-3** display multiple overlapping bands similar to those of ***t*-2** and ***t*-3**.[15] The oscillator strengths of all three compounds, ***c*-2**, ***c*-3**, and ***c*-4** are reduced (Table 1), and the bands themselves show small solvatochromic shifts (4−5 nm) when the solvent polarity is increased from cyclohexane to acetonitrile (Table 1). The oscillator strengths of the *cis*-aminostilbenes were calculated from the molar absorptivity curves by integration of the longest wavelength absorption band. To calculate the oscillator strengths of the bands of ***c*-2** and ***c*-3**, an assumption was made that the longest wavelength band has Gaussian shape (Figure 1).[18]

Fluorescence Spectroscopy. The weak fluorescence observed for ***c*-3** in cyclohexane or acetonitrile solution at room temperature has a spectrum identical to that of ***t*-3**. This fluorescence might result from either excitation of traces of ***t*-3** present as an impurity (ca. 1%) in our sample of ***c*-3** or from adiabatic formation of singlet ***t*-3** from ***c*-3**. Saltiel and co-workers have shown that adiabatic formation of ***t*-1** and *trans*-1-(2-naphthyl)-2-phenylethylene from the corresponding cis isomer can occur in the excited state, resulting in the observation of trans fluorescence upon excitation of the cis isomer.[3,13] Such adiabatic conversion would result in the observation of ***t*-3** fluorescence upon excitation of ***c*-3**. To avoid observation of emission from ***t*-3**, the fluorescence spectra of ***c*-3** have been measured at low temperatures in rigid matrices which should prevent large amplitude geometry changes such as cis−trans photoisomerization.

The fluorescence spectra of ***c*-3** at 77 K in a methylcyclohexane (MCH) or 2-methyltetrahydrofuran (MTHF) glass are red shifted relative to the ***t*-3** emission in accord with previous observations of substituted *cis*-stilbene fluorescence spectra (Table 1).[10,11] The integrated intensity of the fluorescence decreases as the temperature is increased. However, quantitative information about the fluorescence quantum yield could not be obtained above 160 K since the spectra contain a significant contribution from the much more strongly fluorescent ***t*-3**. Below 160 K, the fluorescence maxima of ***t-3*** shifts substantially making it difficult to deconvolute the trans fluorescence from that of the cis isomer. The temperature dependence of the band maximum of the fluorescence spectra of ***t*-3** in MTHF has been discussed and similar red shifts are observed for ***c*-3** on initial cooling until the glass transition temperature below which an abrupt blue shift is observed.[15] This behavior has been found to correlate with the bulk dielectric constant of the MTHF.[19]

In the case of ***c*-2** and ***c*-4**, only weak emission was observed at low temperatures in MCH or MTHF glasses. This emission was found to be identical to that of the corresponding trans isomers which are highly fluorescent at 77 K.[15] Even though the trans isomer was present in <2%, the observed fluorescence was entirely that of the trans isomer. This suggests that the fluorescence quantum yields of ***c*-2** and ***c*-4** are quite low ($\Phi_f < 10^{-3}$), even at 77 K so that only fluorescence from the trans isomer is observed.

Singlet Lifetimes. The singlet lifetime of ***c*-1** in nonpolar solvents at room temperature is 1.03 ps[6] and increases to 4.7 ns in a 3-methylpentane glass at 77 K.[20] The singlet lifetime of ***c*-3** is 17.4 ns at 77 K in a MTHF glass as measured either by time-resolved fluorescence decay or by ns transient absorption spectroscopy probing at 430 nm, near the maximum in the transient absorption spectrum of ***c*-1**.[7] In the case of ***c*-2** and ***c*-4**, singlet lifetimes could not be measured since there was no detectable fluorescence from either compound at 77 K in a MTHF glass. Attempts to determine their singlet lifetimes by means of ps time-resolved transient absorption spectroscopy in a MTHF glass at 77 K were also unsuccessful. Only the transient signal of the singlet trans isomers was observed for both ***c*-2** and ***c*-4**. Thus, either the absorbance of the singlet cis isomers is very low or their decay is too rapid to permit detection in the presence of the strongly absorbing trans impurities.

The temperature dependence of the singlet lifetime of ***c*-3** was studied between 77 and 200 K (Table 2 and Figure 2). The lifetimes are dual exponential over the entire temperature range, one component decreasing with increasing temperature and the other component remaining constant at 14.5 ns above 100 K. The former component is assigned to ***c*-3**, whereas the latter is assigned to ***t*-3** present as a minor (<2%) although highly fluorescent impurity. The ratio of the cis/trans fluorescence components was found to decrease as the temperature is raised, consistent with a low fluorescence yield for ***c*-3** that is strongly temperature dependent (Figure 2, inset). It is to be noted that although two conformers of ***c*-3** are predicted to exist, triple exponential decays were not observed suggesting that either the lifetimes of the two conformers are similar to the time resolution of our apparatus (1 ns) or only one conformer is fluorescent. The lack of temperature dependence of the singlet lifetime of ***t*-3** has been shown to be due to the existence of a large barrier to photoisomerization on the singlet potential energy surface.[15]

The lifetime data for ***c*-3** was fit to a function that contained only one activated process (eq 1) although it would be expected that there should be two activated processes leading to photoi-

TABLE 1: Spectroscopic Parameters for *c*-1−*c*-4

		absorption maximum (λ_{max}/nm)	molar absorptivity (log ϵ_{max})	fluorescence maximum (λ_{max}/nm)	0−0 transition (λ/nm)	stokes shift (cm^{-1})	oscillator strength (f)
***c*-1**	cyclohexane	276	4.03[c]	440[a,d]	353[d]	5600[d]	0.34[c]
	acetonitrile	276	4.05	420[b]	345[b]	5332[b]	0.35
***c*-2**	cyclohexane	238, 279, 322	4.16, 3.89, 3.63	n.f.[e]	n.f.	n.f.	0.08
	acetonitrile	238, 278, 322	4.22, 3.90, 3.66	n.f.	n.f.	n.f.	0.10
***c*-3**	cyclohexane	246, 283, (315)[f]	4.27, 3.95, (3.54)	439[a]	372[a]	4406[a]	0.07
	acetonitrile	238, 276, (320)[f]	4.28, 4.01, (3.54)	429[b]	382[b]	3345[b]	0.05
***c*-4**	cyclohexane	302	4.22	n.f.	n.f.	n.f.	0.45
	acetonitrile	306	4.16	n.f.	n.f.	n.f.	0.41

[a] Fluorescence spectrum in methylcyclohexane at 77 K. [b] Fluorescence spectrum in MTHF at 77 K. [c] Reference 35. [d] Reference 11, the fluorescence maximum at room temperature in *n*-hexane is 404 nm[3]. [e] n.f.: nonfluorescent. [f] Shoulder.

TABLE 2: Low-Temperature Singlet Lifetimes for *c*-3 in MTHF

temperature (K)	τ_1 (ns)[a]	A_1	τ_2 (ns)[a]	A_2
77	17.4	0.156	12.3	0.193
100	16.3	0.117	9.6	0.232
120	14.7	0.016	14.7	0.016
140	10.0	0.149	14.5	0.149
160	5.5	0.022	15.1	0.072
180	2.3	0.069	14.4	0.148
200	1.9	0.146	14.4	0.200

[a] Error is approximately 1.0 ns.

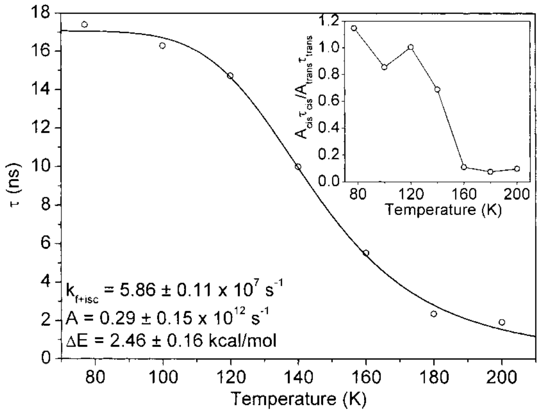


Figure 2. Temperature dependence of the singlet lifetime of ***c*-3** in MTHF. Ratio of the cis/trans fluorescence is shown in the inset.

somerization and photocyclization (Scheme 1).

$$\tau = \frac{1}{\sum_i k_i + \sum_j A_j e^{-\frac{\Delta E_j}{RT}}} \tag{1}$$

An activation energy of 2.5 kcal/mol with a preexponential factor of 2.9 × 10^{11} s^{-1} is obtained from eq 1 with the sum of the rate constants for fluorescence and intersystem crossing being 5.9 × 10^{7} s^{-1}. If the rate of intersystem crossing is assumed to be approximately 4.0 × 10^{7} s^{-1}, then the calculated rate constant of fluorescence is 2 × 10^{7} s^{-1}. Fitting the data to two activated processes gives two sets of activation parameters that are either identical or one of the preexponential factors is unreasonably small indicating that the activated process would have a negligible rate constant. It is always possible to fit multiple processes with similar activation parameters to a model with only one activated process (see Supporting Information, Figures S1−S4). This suggests that the photoisomerization and photocyclization processes in ***c*-3** have similar activation parameters, as previously observed by Muszkat for a series of substituted *cis*-stilbenes.[21] However, the similarity of the activation parameters for the two processes does not require that they arise from a common intermediate or even the same rotamer.[3] Therefore, these activation parameters should be considered as representative of the actual activation parameters for photoisomerization and photocyclization. The large activation energy for photoisomerization in ***c*-3** is particularly notable. In the case of *cis*-stilbene, Saltiel and co-workers have shown that the 0.33 kcal/mol barrier observed in hexane solution is in fact a solvent-induced barrier and that the reaction has a negative intrinsic barrier.[3] The excited singlet potential energy surface of ***c*-3** therefore appears to be strongly perturbed by the amino substituent as in the case of ***t*-3**.[15]

TABLE 3: Radiative Rate Constants Based on the Strickler−Berg Equation[a]

	***c*-1**	***c*-2**	***c*-3**	***c*-4**
cyclohexane	1.64 × 10^{8} [a]	n.f.[b]	3.2 × 10^{7}	n.f.
acetonitrile/MTHF	1.57 × 10^{8}	n.f.	2.5 × 10^{7}	n.f.

[a] Experimental k_f is 8.0 × 10^{7} s^{-1}. [b] n.f.: nonfluorescent.

Radiative Rate Constants. The radiative rate constants for ***c*-3** can be estimated using the 77 K fluorescence spectrum in a MCH or MTHF glass. However, since ***c*-2** and ***c*-4** do not fluoresce, it is not possible to estimate radiative rate constants for these compounds. It should be pointed out that the experimental radiative rate constant for *cis*-stilbene (8.0 × 10^{7} s^{-1}) measured by Saltiel and co-workers[3] is lower than that estimated via the Strickler−Berg equation[22,23] (1.4 × 10^{8} s^{-1}, eq 2):

$$k_f = 2.889 \times 10^{-9} n^2 \cdot \frac{\int_0^\infty f(\bar{\nu})\,d\bar{\nu}}{\int_0^\infty f(\bar{\nu})\bar{\nu}^{-3}\,d\bar{\nu}} \int_0^\infty \frac{\epsilon(\bar{\nu})\,d\bar{\nu}}{\bar{\nu}} \tag{2}$$

where n is the refractive index of the solvent and $f(\bar{\nu})$ and $\epsilon(\bar{\nu})$ are the fluorescence intensity and molar extinction coefficient curves in wavenumbers (cm^{-1}). Such discrepancies between experimental and calculated radiative rate constants may be due to relaxation processes occurring in the S$_1$ state leading to a substantially different geometry than the ground state.[22] Evidence that geometry changes do in fact occur in the excited state of *cis*-stilbene is provided by the large Stokes shifts that *cis*-stilbene displays relative to *trans*-stilbene.[13]

The calculated radiative rate constants for ***c*-3** in nonpolar and polar solvents are given in Table 3. It is seen that in both solvents, the rate constant is much lower than that for ***c*-1** due to the reduced oscillator strength of the $S_0 \rightarrow S_1$ transition in ***c*-3** (Table 1). Experimentally, this would manifest itself in lower fluorescence quantum yields and longer singlet lifetimes for a given set of activation parameters. As previously noted, the singlet lifetime of ***c*-3** at 77 K in MTHF is 17.4 ns, much longer than the 4.7 ns lifetime for ***c*-1**.[20] The calculated radiative rate

TABLE 4: Quantum Yields for Photoisomerization and Photocyclization

		c-1	c-2	*c*-3	*c*-4
ϕ_{isom}	cyclohexane	0.35	0.48	0.07	0.37
	acetonitrile		0.44	0.07	0.42
ϕ_{cycl}	cyclohexane	0.10[a]	<0.002	0.28[a]	0.004[b]

[a] From reference 21. [b] From reference 8.

constant and singlet lifetime provide a fluorescence quantum yield of 0.56 in MTHF at 77 K.

Photoisomerization Quantum Yields. The cis−trans photoisomerization quantum yield (ϕ_i) of *cis*-stilbene has been measured in methylcyclohexane/isohexane at room temperature and found to be lower (0.35) than that of *trans*-stilbene (0.50) under identical conditions due to the competing dihydrophenanthrene photocyclization which also occurs from the S_1 state in *cis*-stilbene.[17] The measured cis,trans photoisomerization quantum yields for ***c*-2**, ***c*-3**, and ***c*-4** in cyclohexane and acetonitrile at room temperature are presented in Table 4. It is seen that the quantum yields vary quite widely, although solvent polarity does not appear to affect the quantum yields substantially.

The cis,trans photoisomerization quantum yields for ***c*-2** are nearly 0.5 ($2\phi_i = 0.88$ in cyclohexane and 0.96 in acetonitrile) suggesting that the photocyclization reaction does not compete effectively with cis,trans isomerization. Significantly, no dihydrophenanthrene formation is observed spectroscopically when nitrogen purged or undegassed solutions of ***c*-2** in either cyclohexane or acetonitrile are irradiated at 300 nm.[24] The failure to observe dihydrophenanthrene formation indicates that either the cyclization process is highly inefficient or that the product reverts rapidly to starting material. Aminophenanthrene formation occurs in low yield only after prolonged irradiation in aerated solutions in the absence of added iodine.[25]

In the case of ***c*-3**, the cis−trans photoisomerization quantum yield ($2\phi_i = 0.14$ in cyclohexane and acetonitrile) is unusually low, suggesting that photocyclization is the predominant decay pathway for the excited singlet state. Experimentally, Güsten and co-workers have determined the quantum yield of photocyclization for ***c*-3** to be ≥0.28 in cyclohexane,[8,9] the largest value reported for a monosubstituted *cis*-stilbene (Table 4).[8] At room temperature, the photochemistry of ***c*-3** is dominated by two processes: photocylization and photoisomerization. The quantum yield for formation of the intermediate leading to dihydrophenanthrene (DHP* in Scheme 1)[5,26] is therefore 0.86 ($1 - 0.7 \times 2$). This value and the photocyclization quantum yield provide a branching ratio of 2.1:1 for partitioning of this intermediate between dihydrophenanthrene and ground state ***c*-3**. This value is similar to that determined for ***c*-1** (2:1).[3]

Two aminophenanthrene products are obtained from irradiation of ***c*-3** in the presence of oxygen (Scheme 2). The ratio of the two products was assumed by Güsten et al. to be 1:1.[8] However, we find that the ratio is dependent on the amount of oxygen present in accord with a prior study by Somers and Laarhoven[27] on a series of meta substituted *cis*-stilbenes. Irradiation of undegassed solutions of ***c*-3** in acetonitrile yields a ca. 3:1 ratio of 2-aminophenanthrene:4-aminophenanthrene.[28] However, other factors that may affect the product ratio such as excitation wavelength, oxidant, solvent, and temperature were not investigated.

The cis−trans photoisomerization quantum yield for ***c*-4** ($2\phi_i = 0.74$ in cyclohexane and 0.84 in acetonitrile) is slightly larger than that of *cis*-stilbene ($2\ \phi_i = 0.70$ in cyclohexane) suggesting that the partitioning of the excited singlet state between photoisomerization and photocyclization may be similar to that of *cis*-stilbene. However the measured photocyclization quantum yield for ***c*-4** is much lower than that for *cis*-stilbene (Table 4).[8,9,21] As in the case of ***c*-2**, the low photocyclization quantum yield for ***c*-4** may be due to either rapid reversion of the dihydrophenanthrene intermediate back to ground state ***c*-4** or inefficient trapping of the intermediate by oxygen.

Potential Energy Surfaces for the *cis*-Aminostilbenes. The potential energy surface for singlet *cis*-stilbene has been discussed by Saltiel and is characterized by essentially barrierless cis,trans photoisomerization[3] and weakly activated photocyclization (Figure 3).[21] The 0−0 energy for *cis*-stilbene is reported to be 85.7 kcal/mol at room temperature in *n*-hexane and ≤83.3 kcal/mol for jet cooled *cis*-stilbene in an Ar cluster.[3,29] In the case of ***c*-2** and ***c*-4**, it is not possible to determine the 0−0 energies as fluorescence is not detected for these compounds even at 77 K. For ***c*-3**, a 0−0 energy of 76.9 kcal/mol in nonpolar solvents is determined from the absorption spectrum in cyclohexane and the fluorescence spectrum in methylcyclohexane at 77 K. The 0−0 energy for ***c*-3** is lower than that of *cis*-stilbene as a result of stabilization of the excited singlet state resulting from configuration interaction rather than from resonance stabilization by the meta amino substituent.[15]

Torsion about the *cis*-stilbene double bond results in the formation of the same perpendicular intermediate P* as that formed from torsion of the trans isomer (Figure 3). The analogous P* state for the aminostilbenes is accessible from ***c*-3** as well as ***t*-3**.[15] The P* state is expected to be zwitterionic[30,31] for a donor-substituted stilbene, however the meta amino substituent would be expected to offer little resonance stabilization to the meta aminobenzyl cation[32] fragment. Thus, the energy of the S_1 state but not the P* state is lowered by the meta amino substituent resulting in a torsional barrier that is larger than that for other monosubstituted *cis*-stilbenes (Figure 3). Experimentally the barrier for cis−trans photoisomerization is approximately 2.5 kcal/mol. While this barrier is smaller than that for photoisomerization of ***t*-3** (> 7 kcal/mol), it is larger than that for ***c*-1**.[15]

On the basis of the quantum yields reported for ***c*-1**, it is expected that the preexponential factor for the photocyclization reaction is larger than that for photoisomerization since it competes with cis−trans photoisomerization despite having a larger effective activation barrier (1.2 kcal/mol vs 0.33 kcal/mol).[3,33,34] Therefore, the large photocyclization quantum yield and low cis,trans photoisomerization quantum yield for ***c*-3** at room temperature may be the result of an unusually large barrier on the excited singlet surface for photoisomerization as well as a larger preexponential factor for the photocyclization reaction.

By contrast, the photochemistry of ***c*-2** and ***c*-4** is dominated by photoisomerization. In the case of ***c*-4** ($2\phi_i \geq 0.74$), the extent of cis,trans photoisomerization is similar to that of ***c*-1**, however, the quantum yield for phenanthrene formation is lower than that observed for ***c*-1**. The similarity of the photoisomerization quantum yields suggest that barrierless torsion in the excited singlet state of ***c*-4** is similar to that in ***c*-1** (Figure 3). Thus, the para amino substituent does not increase the torsional barrier for either ***c*-4** or ***t*-4**.[15] The low photocyclization efficiency may reflect either unfavorable partitioning of DHP* between starting material and DHP (Figure 3) or inefficient oxidation of DHP to the aminophenanthrene.

Cis−trans photoisomerization also accounts for most of the excited-state decay in ***c*-2** ($2\phi_i \geq 0.88$). This suggest that barrierless torsion about the double bond occurs in the excited singlet state of ***c*-2**, unlike ***t*-2** for which a large torsional barrier (>7 kcal/mol) was observed.[15] The large barrier for ***t*-2** was

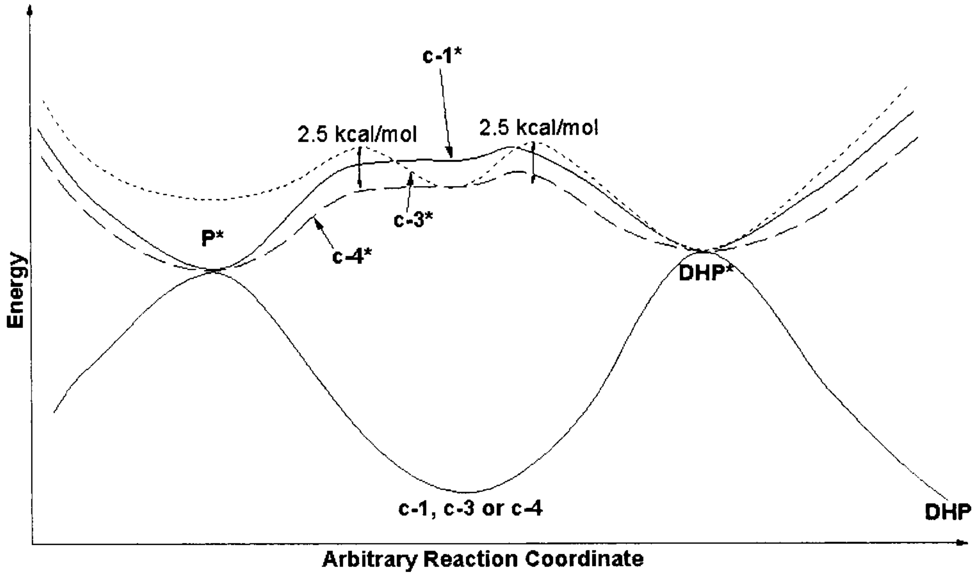
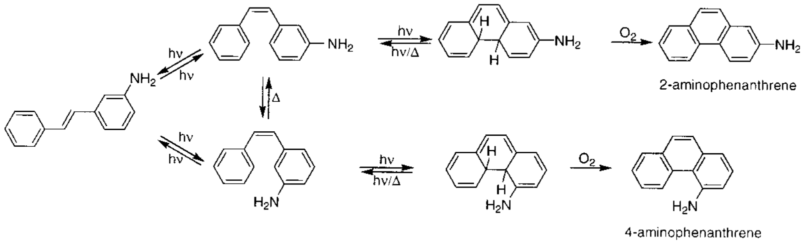


Figure 3. Simplified potential energy surface of ***c*-1** (solid line), ***c*-3** (short dashes) and ***c*-4** (long dashes). The potential energy surface for ***c*-2** is similar to that of ***c*-4** with a larger barrier for the formation of DHP*. The energies of the P* and DHP* states are assumed.

SCHEME 2



attributed to greater stabilization of the planar S_1 state (resulting from strong configuration interaction) than the twisted P*. The energy of the highly nonplanar S_1 state of ***c*-2** may be substantially higher than that of ***t*-2** resulting in exergonic, barrierless formation of P*.

Nonradiative Decay: No fluorescence is observed from ***c*-2** or ***c*-4** even at 77 K suggesting that either a temperature independent nonradiative channel is operational or that the intersystem crossing rate constants are unusually large. Similar observations of nonfluorescent *cis*-stilbenes have been made by other workers.[11,35−38] For instance, Hohlneicher and co-workers have noted that 1,2-diphenylcyclohexene is nonfluorescent in a 3-methylpentane glass at 77 K, as an isolated molecule, or in Ar clusters.[35−37] It was suggested that a low oscillator strength benzenic L_b state was the lowest state and therefore small radiative rate constants and low fluorescence quantum yields were expected.[35] However, such a state should have a long singlet lifetimes at 77 K in the absence of a nonradiative channel. Another explanation proposed was that torsion about the double bond is involved in a nonradiative channel particularly since the cyclobutene ($\phi_f = 1.0$[39] at room temperature) and cyclopentene ($\phi_f = 0.9$[34] at 93 K) analogues were found to be highly fluorescent.[35] The measured singlet lifetime of 1,2-diphenylcyclohexene at room temperature is <20 ps,[40] and since no low-temperature singlet lifetimes are available, it is not possible to distinguish between these two explanations for the absence of fluorescence at low temperature.

A nonradiative channel involving photocyclization is the major decay pathway for 1,2-diphenylcyclohexene at room temperature but is unlikely at low temperatures due to the high viscosity of the medium.[3,21,33] The orientation of the two phenyl rings apparently plays an important role in determining the activation barrier for photocyclization and is optimal for 1,2-diphenylcyclohexene.[36,37] As a result, this process has been determined to occur without an activation barrier for 1,2-diphenylcyclohexene but occurs with a 2.6 kcal/mol barrier for 1,2-diphenylcyclopentene and is restricted for 1,2-diphenylcyclobutene.[36,37] In highly viscous media, DHP formation may be inhibited, however, formation of the intermediate DHP* (Figure 3) may still occur in 1,2-diphenylcyclohexene due to its optimal geometry.[26] This intermediate could then revert to the ground state 1,2-diphenylcyclohexene resulting in efficient quenching of fluorescence even at 77 K.

Other examples of nonfluorescent stilbenes were provided by Muszkat and co-workers who noted that the sum of the fluorescence and photoisomerization quantum yields was <1.0 for either trans-α,α′-difluorostilbene ($\phi_{sum} = 0.57$) or *trans*-α,α′-dichlorostilbene ($\phi_{sum} = 0.16$) in methylcyclohexane/3-methylpentane at 98 K with the fluorescence quantum yields being 0.25 and 0.15 at 77 K, respectively.[11] The fluorescence quantum yield for *trans*-α,α′-dimethylstilbene was found to be 0.04 at 93 K and 0.20 at 77 K indicating the presence of a nonradiative pathway in this compound as well. It was suggested that the remainder of the excited molecules were decaying via a radiationless channel that involved torsion about the double bond or by intersystem crossing but without photoisomerization.[11] Görner and Schulte-Frohlinde have demonstrated that in the case of *trans*-4-chlorostilbene no enhanced intersystem crossing is observed, indicating that it may not be a significant pathway for either α,α′-difluorostilbene or α,α′-dichlorostilbene.[41] Wismonski-Knittel and Fischer have shown that *cis*-1-

(2-naphthyl)-2-(2-benzo[*c*]phenanthryl)ethylene is nonfluorescent at 93 K in methylcyclohexane/isohexane.[38]

For ***c*-2** and ***c*-4** the upper limit for the quantum yields of fluorescence may be estimated such that their fluorescence would be weaker than the fluorescence from ***t*-2** and ***t*-4**, respectively, present as impurities in the cis isomers. The amount of fluorescence observed from either cis or trans isomer is dependent on the isomer composition, molar absorptivities, and fluorescence quantum yields. The fluorescence quantum yields for ***t*-2** and ***t*-4** in MTHF glasses at 77 K are expected to be $>$ 0.8.[15] On the basis of the presence of 2% trans isomer it is estimated that the upper limit for the fluorescence quantum yields for ***c*-2** and ***c*-4** is approximately 0.005. Such low quantum yields require minimum nonradiative rate constants estimated to be 2.0×10^9 s^{-1} and 7.9×10^9 s^{-1} for ***c*-2** and ***c*-4**, respectively, assuming that the radiative rate constants are 2×10^7 and 8×10^7 s^{-1}, respectively, and the intersystem crossing rate constant is 3×10^7 s^{-1} in MTHF, similar to the value in nonpolar solvents.[15,16] The radiative rate constant for ***c*-4** is assumed to be similar to that of *cis*-stilbene based on the similar oscillator strengths of the two compounds. Because of the reduced oscillator strength of ***c*-2**, its radiative rate constant should be even lower than for ***c*-4**. An approximate value of 2×10^7 s^{-1} is assigned based on the rate constant calculated for ***c*-3** using the Strickler−Berg equation.

The existence of a nonradiative channel may be ascribed either to the formation of a cyclized DHP* intermediate that decays to the *cis*-aminostilbene ground state or to nonradiative decay via a limited double bond torsion mechanism, as suggested previously by Fischer.[11] Partial torsion about the double bond would reduce the S_1-S_0 gap, thereby increasing nonradiative decay based on the energy gap law given in eq 3 (Figure 3):[42−44]

$$k_{nr} = 10^{13}e^{-\alpha\Delta E_{0-0}} \tag{3}$$

where k_{nr} is the nonradiative rate constant, α is an empirical parameter, and ΔE_{0-0} is the singlet energy in eV. The empirical parameter α has been estimated to be 4.85 for polyaromatic hydrocarbons based on nonradiative decay data.[43] Using this value for α and the minimum nonradiative rate constants calculated above, minimum energy gaps of 40 and 34 kcal/mol are calculated for ***c*-2** and ***c*-4**, respectively. Reduction of the S_1-S_0 gap may also occur on the photocyclization coordinate, although it has been proposed that a conical intersection exists at the dihydrophenanthrene intermediate (DHP*) geometry which has been calculated by Robb and co-workers to be a biradical with only a slight change in geometry relative to the Franck−Condon geometry of ***c*-1**.[26] Approaching a conical intersection should result in highly efficient nonradiative decay to ground state *cis*-stilbene.

The operation of efficient nonradiative pathways in substituted *cis*-stilbenes would be expected to be sensitive to parameters such as the fluorescence rate constant, the molecular geometry, and the S_1-S_0 gap. A combination of these factor may therefore make efficient nonradiatve decay at 77 K unique to a few *cis*-stilbenes.

Concluding Remarks

The photophysics and photochemistry of *cis*-aminostilbenes hve been studied and found to be similar to those of the corresponding *trans*-aminostilbenes in certain respects. The absorption spectra of the *cis*-aminostilbenes resemble those of the corresponding *trans*-aminostilbenes in appearance, although the intensity of the bands is reduced due to the nonplanarity of the cis isomers. Their spectra are also are blue-shifted, as observed for other substituted *cis*-stilbenes. This suggests that configuration interaction due to loss of symmetry occurs for ***c*-2** and ***c*-3**, as is the case for ***t*-2** and ***t*-3**.[15] Since the same P* state is formed upon torsion of both the cis and trans isomers (Figure 3), stabilization of P* by the amino substituent is not expected for ***c*-2** and ***c*-3**. On the basis of this model, a barrier to singlet state double bond torsion was anticipated for both ***c*-2** and ***c*-3**, as previously observed for ***t*-2** and ***t*-3**.[15] A barrier is observed in the case of ***c*-3**; however, it is considerably smaller than that observed for ***t*-3**. No barrier is observed in the case of ***c*-2**. Reduced configuration interaction due to nonplanarity may result in a S_1 state for ***c*-2** that is not as strongly stabilized as in ***t*-2** and thus eliminate the barrier for torsion in singlet ***c*-2**.

The singlet state of ***c*-3** is strongly fluorescent at 77 K and has an exceptionally long lifetime for a stilbene. However no fluorescence is observed from ***c*-2** and ***c*-4,** possibly due to the existence of an efficient nonradiative channel. Similar nonradiative decay has been observed for several other substituted *cis*-stilbenes and has been attributed to the presence of a decay channel involving restricted double bond torsion or cyclization on the singlet surface.[11,35] Although the exact nature of the nonradiative channel is unclear, the result is a lack of fluorescence even at 77 K. The fact that this channel operates at low temperatures suggests that it does not involve large amplitude nuclear motion. In contrast, no nonradiative decay was observed at 77 K for ***c*-3**. This may be a result of the fact that both ethenyl bond torsion and formation of DHP* are activated processes for ***c*-3** and therefore do not occur at 77 K.

Experimental Section

Material. The *cis*-aminostilbenes ***c*-2**−***c*-4** were prepared using the Wittig procedure of Lee and Marvel.[45] Corresponding *ortho*-, *meta*-, *para*-nitrobenzaldehydes (Aldrich) were reacted with triphenylphosphonium chloride (Aldrich) in a $CH_2Cl_2-H_2O$ dual phase system using tetrabutylammonium iodide (Aldrich) as a phase-transfer catalyst (10 mol %). The reaction mixture was stirred at room-temperature overnight under a N_2 atmosphere. After completion of the reaction, the CH_2Cl_2 layer was separated and washed with brine several times. Purification was carried by column chromatography (SiO_2/hexanes−EtOAc (90:10), 230−400 mesh SiO_2) to remove the trans isomer. Typical overall yields of the cis isomer were 20%. Reduction of the nitro group to the amino group was carried out using Zn/HCl−AcOH as the reducing agent.[46] Typical yields from the reduction were 65%. Purification of the corresponding *cis*-aminostilbene was carried out by repeated column chromatography. If necessary, the cis isomer was enriched by Kugelrohr distillation under high vacuum ($<$0.1 Torr) in the absence of light prior to chromatography. Whereas ***c*-2** and ***c*-4** were found to have greater than 98% purity, ***c*-3** was determined to be 99.6% pure as estimated by GLC. ^{1}H NMR (300 MHz, $CDCl_3$) and HRMS was done to establish that the identity of all compounds. All solvents used for spectroscopy were either spectrophotometric or HPLC grade (Fisher) and were used as received.

Methods. ^{1}H NMR spectra were measured on a Varian Gemini 300 spectrometer. GLC analysis was performed using a Hewlett-Packard HP 5890 instrument equipped with a HP1 poly(dimethylsiloxane) capillary column. UV−vis spectra were measured on a Hewlett-Packard 8452A diode array spectrometer using a 1 cm path length quartz cell. Fluorescence spectra were measured on a SPEX Fluoromax spectrometer. Low-temperature spectra were measured either in a Suprasil quartz EPR tube using a quartz liquid nitrogen coldfinger dewar at 77 K or in a Oxford Cryogenics DN1704 cryostat fitted with a Oxford Instruments ITC4 temperature controller. Fluorescence decays were measured on a Photon Technologies International Timemaster stroboscopic detection instrument with a gated hydrogen or nitrogen lamp using a scatter solution to profile the instrument response function. Nonlinear least-squares fitting of the decay curves were fitted using the Levenburg−Marquardt algorithm as described by James et al.[47] and implemented by the Photon Technologies International Timemaster (version 1.2) software. Goodness of fit was determined by judging the χ^2 ($<$1.3 in all cases), the residuals and the Durbin−Watson parameter ($>$ 1.6 in all cases). Transient absorption decays were measured using a femtosecond amplified Ti:sapphire-based laser system that has been described previously.[48,49] A ca. 200 fs, 331 nm laser pulse is used for excitation and a white light probe pulse of somewhat smaller duration is used to monitor the spectra as a function of time. Measurements of quantum yields of photoisomerization for ***c*-2** and ***c*-3** were measured on optically dense degassed solutions ($\sim 10^{-3}$ M) using an excitation wavelength of 313 nm and the extent of photoisomerization ($<$5%) was quantified using GLC. Quantum yields of photoisomerization for ***c*-4** ($<$10% conversion) were determined by changes in absorbance at 2 wavelengths before and after irradiation at 313 nm. Excitation at 313 nm was achieved using a 150 W medium-pressure mercury arc lamp filtered through an alkaline potassium dichromate solution (***c*-2** and ***c*-3**) or a 150 W xenon lamp filtered through a Bausch and Lomb high-intensity monochromator (***c*-4**). All spectroscopic measurements were performed on solutions that were purged with dry N_2 for 20−25 min. For photocyclization studies, solutions were degassed under vacuum ($<10^{-4}$ Torr) through five freeze pump thaw cycles and flame-sealed to establish the validity of the N_2 purged experiments. Gaussian fitting procedures were carried out using GRAMS/386 (version 3) software on a IBM-compatible PC running Windows NT version 4.0.[50]

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Supporting Information Available: Kinetic modeling of the temperature-dependent singlet lifetimes of ***c*-3** in MTHF. This material is available free of charge via the Internet at http://pubs.acs.org.

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