Remote Substituent Effects on Methyl Torsional Barriers: trans-p-Amino-p'-methylstilbene

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The expansion-cooled fluorescence excitation spectrum of *trans-p*-amino-p'-methylstilbene is presented. It displays several prominent low-frequency modes, including a progression in the methyl torsion. Fits of the torsional progression yield an S₁ barrier of 54 cm⁻¹, which is nearly a factor of 3 lower than the S₁ barrier of the related molecule, *trans-p*-methylstilbene. The lower barrier is attributed to a reduction in the asymmetry of the π electron density at the two positions adjacent to the CH₃ caused by the strongly donating amino group. This is facilitated by delocalization of the π system in the excited state. Other data, such as the behavior of the low-frequency ring motions and the crystal structure, are presented in support of this model.

Introduction

The advent of expansion cooling for the reduction of spectral congestion and the availability of moderate to high resolution laser systems has enabled the study of low-frequency, nonrigid motions in electronically excited states. Of such motions, the hindered internal rotation of methyl groups¹⁻⁵ and the inversion of amino groups⁶⁻⁹ have garnered significant attention. Previously this group reported the π system-mediated interaction of these two moieties in p-toluidine (p-methylaniline).⁶ In pmethylaniline, the interaction is manifested as a quartet splitting of the inversion overtone, I_0^2 (~720 cm⁻¹ frequency), which possesses significant intensity due to a change from a pyramidal amino group geometry in the ground state to a planar geometry in S_1 . The interaction between the methyl and amino groups generates these splittings only when the amino is undergoing large amplitude motion. In this work, we present the fluorescence excitation spectrum and selected single vibrational level dispersed fluorescence spectra of trans-p-amino-p'-methylstilbene in order to address whether such interactions occur over a more extended π system. In addition, remote substitution also addresses the role of π electron effects (as opposed to steric) on the methyl barrier.

Experimental Section

The jet apparatus used to acquire the spectra comprises a 6 in., six-way, stainless steel cross evacuated by a Varian VHS-6 diffusion pump. The samples were heated, entrained in He at 1-3 atm, and expanded through a General Valve pulsed nozzle. The expansion was crossed at 90° by the output from a Lumonics HyperTrack/HyperDye 300/HY-750 Nd:YAG pumped, pulsed dye laser system. The fluorescence was collected by a Melles Griot ellipsoidal reflector and focused onto the photocathode of an EMI 9813QB photomultiplier tube for the fluorescence excitation spectra. For dispersed emission work, the slit of a 0.25 m Oriel monochromator with a 2400 lines/ mm grating was placed at the focus.

The *trans-p*-amino-p'-methylstilbene was synthesized by first preparing *trans-p*-nitro-p'-methylstilbene from 1-bromomethyl-4-nitrobenzene via a Wittig process. The nitro group was then reduced with powdered tin in an HCl solution. The single crystal used for the X-ray diffraction work was prepared by vapor diffusion of methanol containing *trans-p*-amino-p'methylstilbene into water.

Results and Interpretation

The expansion-cooled, fluorescence excitation spectrum of *trans-p*-amino-p'-methylstilbene (AMeS) is presented in Figure 1. The origin appears as a doublet due to the $0a_1-1e$ tunneling splitting of the hindered internal rotation of the methyl group. The methyl torsion is also responsible for much of the low-frequency structure in the spectrum, which will be discussed in detail later. The splitting and torsional progression will typically appear in combination with the skeletal modes of the molecule. Hence, skeletal vibrational bands should appear as doublets with a splitting and intensity ratio similar to that of the origin.

Skeletal Modes. A weak doublet is observed at 89 cm^{-1} , which we assign as 37_0^2 by analogy with the 95 cm⁻¹ transition in trans-stilbene^{10,11} (tS) and the 90 cm⁻¹ band in trans-pmethylstilbene (MeS).² In Warshel's QCFF-PI calculation,¹² v_{37} is the phenyl torsion that distorts the stilbene rings into a propeller-like geometry (see Figure 2). Dispersed fluorescence from this doublet shows a progression of very low frequency transitions with an approximately 20 cm⁻¹ spacing, consistent with DF from 37_0^2 in both tS and MeS. It should be noted that more recent work by Chiang and Laane¹³ (C&L) assigns the 95 cm⁻¹ transition in tS as 36_0^2 , and instead assigns 37_0^2 (which they label as 37_0^3 and 37_0^4 owing to each level's double degeneracy) to the 70 cm^{-1} transition. We disagree with this assignment. Para substitution should have a large effect on the reduced mass for v_{36} because of the out-of-plane motion of that ring position. In contrast, para substitution with either CH₃ or NH₂ should have a small effect on the ring torsion mode, v_{37} , because the heavy atoms lie on the torsional axis and will not contribute to the reduced moment of inertia. The 90 and 89 cm⁻¹ transitions in MeS and AMeS, respectively, are consistent with assignment of these and the 95 cm^{-1} band in tS as 37_0^2 , especially given that they all display similar dispersed fluorescence spectra.

The 37_0^2 band is noticeably weaker in AMeS than the analogous band in *trans*-stilbene, which may case some doubt on the assignment. Since this is an out-of-plane mode in a molecule that is planar in both states, there is no displacement and the observed intensity must come from the difference in frequency (width of the potential well) between the electronic states. In *trans*-stilbene, 37_1 has a frequency of $9-10 \text{ cm}^{-1}$ and can be easily populated in the jet when mild expansion conditions are used. Figure 3 shows the jet spectrum of AMeS under two different expansion conditions. The warmer spec-

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Figure 1. Jet-cooled fluorescence excitation spectrum of *trans-p*-amino-*p*'-methylstilbene. The 0_0^0 band has an absolute frequency of 29 470 cm⁻¹. Tie lines indicate methyl torsional structure at the origin and in combination with several skeletal modes.

trum, taken with significantly lower backing pressure, displays a new transition at 33 cm⁻¹, which we assign as 37¹₁. Since ν_{37} is nearly harmonic in the excited state of tS, we can use this transition to estimate the frequency of 37₁ in AMeS as ~12 cm⁻¹ (89/2 - 33). We can use the Franck–Condon expressions for distorted but not displaced oscillators to determine whether the changes in 37²₀ intensity between molecules are reasonable. For a harmonic oscillator, the appropriate intensity expressions are¹⁴

$$\operatorname{Int}_{0}^{0} \propto \frac{2\sqrt{\omega'\omega''}}{(\omega'+\omega'')} \qquad \operatorname{Int}_{0}^{2} \propto \frac{1}{2} \left(\frac{\omega''-\omega'}{\omega''+\omega'}\right)^{2}$$

For *trans*-stilbene, with $\omega'' = 9 \text{ cm}^{-1}$ and $\omega' = 47.5 \text{ cm}^{-1}$, 37_0^2 is calculated to have 37% of the origin's intensity. In AMeS ($\omega'' = 12 \text{ cm}^{-1}$, $\omega' = 44.5 \text{ cm}^{-1}$), the 37_0^2 intensity is calculated at 20%. While the equations given are not fully appropriate as ν_{37} has significant anharmonicity in the ground state, the calculation does demonstrate that significant intensity differences are expected for small changes in the ν_{37} frequency and that the assignment in AMeS is reasonable. The fact that in AMeS, compared to tS, the S₀ ν_{37} frequency is increased but the S₁ frequency is decreased suggests that the changes are at least partially due to bond order and are not entirely a mass effect.

The most prominent vibration appears at 173 cm⁻¹ with overtones at 347 and 524 cm⁻¹. We assign the 173 cm⁻¹ transition as 25_0^1 , the in-plane, totally symmetric phenyl wag, also by analogy with tS and MeS.^{10,11} This is the lowest frequency A_g mode calculated by Warshel for the C_{2h} transstilbene (tS).¹² Chiang and Laane assign the analogous transi-



v24 Ce-Phenyl Bend

V25 Phenyl Wag



v36 Phenyl Flap

v37 out-of-plane Phenyl Torsion





Figure 3. Low-frequency region of the *trans-p*-amino-p'-methylstilbene fluorescence excitation spectrum taken under different expansion conditions. Note the increase in the 37_1^1 intensity under warmer conditions in the top trace.

tion at 198 cm⁻¹ in tS as 35_{0}^{2} , two quanta of the symmetryforbidden ethylenic torsion. Dispersed emission from this band indicates that the analogous ground state level has a 202 cm⁻¹ frequency. This is a very intense transition, with the band in the excitation spectrum having well over 50% of the origin's intensity. The assignment as an out-of-plane mode is inconsistent with the observed intensity, which must be derived from a frequency difference because there is no displacement in any out-of-plane mode for this molecule, which is known to be planar in both states.^{3,10} The small (~2%) frequency difference simply is not sufficient to generate the observed intensity for this nearly harmonic mode, as can be discerned from the



Figure 4. Comparison of the methyl rotor progressions in *trans-p*-methylstilbene and *trans-p*-amino-p'-methyl-*trans*-stilbene. The barrier decreases by nearly a factor of 3 with amino substitution.

preceding equations. For this reason, we support the previous assignment of this band as 25_0^1 .

Other skeletal modes are observed at 241, 440, 610, and 730 cm⁻¹. We tentatively assign the 241 cm⁻¹ band as Warshel's ν_{24} . An analogous transition is observed in a number of other substituted stilbenes. The 440 cm⁻¹ transition might be 71₀¹, a b_u vibration in the C_{2h} trans-stilbene but a totally symetric a' mode in the planar AMeS.

Methyl Torsion. The origin's doublet at -1.8 and 0 cm⁻¹ relative frequency and the bands at 29.1 and 61.1 cm⁻¹ in the excitation spectrum (Figure 4) can be assigned as methyl torsional transitions. These levels can be fit using a particle in a ring basis set with a potential of the form

$$V = \frac{V_3}{2} [1 - \cos(3\theta)] + \frac{V_6}{2} [1 - \cos(6\theta)] + \dots$$

Diagonalization yields energy levels in the order $0a_1$, 1e, 2e, $3a_2$, $3a_1$, 4e, 5e, ..., where the levels are labeled according to the particle in a ring quantum number and the symmetry under the G₆ molecular symmetry group. The e levels are doubly degenerate, the torsional selection rule for electronic transitions is like symmetry to like symmetry, and the a_2 levels typically are not observed in jet spectra because the lowest a_2 levels usually will not be populated. We assign the transitions at -1.8, 0, 29.1, and 69.1 cm⁻¹ as 1e, $0a_1$, 2e, and $3a_1$, respectively, and can fit these levels with $V_{3'} = 54 \pm 2$ cm⁻¹ and $V_{6''} = -2.7 \pm 1$ cm⁻¹ (see Table 1). These assignments are confirmed by dispersed fluorescence (Figure 5), which readily identifies the symmetry of the excited band owing to the like-like selection rule. In the emission spectra from e symmetry levels, the 2e level of the ground state is 22 cm⁻¹ from the resonance

 TABLE 1: Observed and Calculated Frequencies for the Methyl Rotor Torsional Transitions for trans-p-Amino-p'-methylstilbene^a

	S ₀		S1	
assignment	obs (cm ⁻¹)	calcd (cm ⁻¹)	obs (cm ⁻¹)	calcd (cm ⁻¹)
0a1	0	0	0.0	0.0
1e			-1.8	-1.8
2e	22	21.2	29.1	29.1
$3a_1$	52	51.9	61.1	61.1
4e	82	84.2	91.0	89.8

$${}^{a}F' = F'' = 5.4 \text{ cm}^{-1}$$
; $V_{3}'' = 27 \text{ cm}^{-1} V_{3}' = 53.8 \text{ cm}^{-1}$; $V_{6}' = -2.7 \text{ m}^{-1}$.



Figure 5. Dispersed fluorescence from the methyl torsion bands.

peak. The $3a_1$ level has a frequency of 52 cm^{-1} in the ground state. From these frequencies, we can roughly fit the barrier to internal rotation in S_0 as well (Table 1) and find that $V_3'' \approx 27 \pm 4 \text{ cm}^{-1}$. A value of $F = 5.4 \text{ cm}^{-1}$ was used for the internal rotation constant for both states. Because of the small number of levels fit, slightly different F values can also yield good fits with slightly different potential terms; however, these lie within the error bars given.

Discussion

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The measured S₀ barriers of *trans-p*-methylstilbene and *trans-p*-amino-*p'*-methylstilbene are quite similar, 30 and 27 cm⁻¹, respectively, and the difference is comparable to experimental error, given the relatively poor, monochromator dependent resolution in the measurement of the ground state levels. In sharp contrast, the S₁ barriers to methyl rotation are nearly a factor of 3 different, with MeS having a barrier of 150 cm⁻¹ and AMeS one of 54 cm⁻¹. Given the large distance between the amino substituent and the CH₃, and the surprising magnitude of this effect, it would appear that the π system of the molecule is involved in barrier reduction. In order to understand this



Figure 6. HOMO and LUMO orbitals for stilbene calculated using the AM1 hamiltonian. Only the tops of the carbon p orbitals are pictured. Note the difference in C_e -Ph bonding characteristics between the orbitals.

involvement, it is important to understand the nature of the *trans*stilbene π system in both the ground and excited states.

Semiempirical calculations on tS, MeS, and AMeS all show qualitatively similar orbitals for the HOMO and LUMO, as pictured in Figure 6. The π antibonding nature of the HOMO, combined with the lower energy π MOs, results in a C_e-Ph bond order that is very nearly 1. This means that the π electrons in the S₀ state are not very delocalized over the ethylenic linkage. If the excitation involves HOMO \rightarrow LUMO as the dominant configuration, the antibonding character between the ethylene and phenyl will be reduced by removing an electron from the HOMO, and the C_e -Ph *bonding* character will be increased by partially occupying the LUMO. Stated differently, a HOMO to LUMO excitation transfers π density from the C_e=C_e bond to the two C_e -pH bonds, and the excited state should be considerably more delocalized than the ground state, if this is a dominant configuration in the description of S_1 . Because of the ring torsional nature of the mode, the behavior of v_{37} is a good measure of the Ce-Ph bond order. In the three stilbenes mentioned here, tS, MeS, and AMeS, there is a very low frequency in the ground state for this mode and a factor of 4-5increase in the v_{37} frequency in S₁, indicating a dramatic increase in the Ce-Ph bond order upon excitation, consistent with the excited state description mentioned earlier. These differences are important to the understanding of the relatively low barrier for the S_0 state of MeS compared to that of S_1 . If there is very little delocalization, the methyl-substituted ring should behave similarly to toluene and a low barrier should be observed.¹⁵ Furthermore, because of the lack of delocalization, any changes made to the remote ring should not have a large effect on the π system of the methyl-substituted ring in the ground state. In S_1 , on the other hand, there is significant delocalization, and the existence of the ethylenic group and the remote ring should cause changes in the π system so that the barrier should be different than the S_1 barrier of toluene. Indeed it is 125 cm⁻¹ higher. Also, any changes to the remote ring can be transmitted to the methyl-substituted ring in the excited state, so that remote ring substituent dependencies of the barrier are expected to be significantly greater in S_1 , as observed.

The behavior of other skeletal modes also supports this thinking. Quanta in any of the large amplitude ring motions cause subtle changes in the tunneling splitting and in the frequencies of the other torsional bands. For example, close inspection of 25_0^1 and 25_0^2 reveals a reduction in the methyl tunneling splitting, with the 1e level appearing as a barely resolved shoulder on the low-frequency side for 25_0^2 . This behavior is consistent with the assertion that the π electrons influence the methyl barrier. Changes in the stilbene bond angles as a result of the relatively large amplitude ring motions should have small effects on the π distribution of the stilbene, and specifically in the methylated ring. Presumably, the subtle changes in barrier are in response to the electron density changes.

The effect of the amino group on the π system of the molecule can be addressed by considering the likely geometry of the group. In aniline and p-methylaniline, the inversion band I_0^2 appears prominently in the $700-800 \text{ cm}^{-1}$ region. Additionally, the hot band, I_1^1 , appears at ~300 cm⁻¹ and can be induced to have considerable intensity under mild expansion conditions owing to the low ($\leq 40 \text{ cm}^{-1}$) fundamental frequency of I₁ caused by the inversion tunneling splitting. This distinctive band, which appears in all of the substituted anilines studied in our laboratory, is absent from the 300 cm⁻¹ region of the warm AMeS system. The 730 cm⁻¹ band in AMeS might be I_0^2 , but it is substantially weaker than I_0^2 in *p*-methylaniline and we would not be able to make such an assignment with confidence. Additionally, the dispersed fluorescence spectrum from the origin does not exhibit a strong I_2 band in the 420 cm⁻¹ region, as is characteristic in the anilines. The lack of Franck-Condon activity in AMeS in the inversion mode prevents identification of the sort of dynamic interaction between the NH₂ and CH₃ groups as observed in *p*-methylaniline and leads us to believe that the amino group has the same geometry in both the ground and excited states. Even with the same geometry, the I_1^{I} transition should have reasonable Franck-Condon overlap so we attribute the lack of I_1^1 intensity to low population of the I_1 level. For the pyramidal amino, I_1 is ~ 32 cm⁻¹ and easy to populate, but for the planar amino, one quantum is on the order of 270 cm⁻¹ and would not have significant population in a jet even under the mildest expansion conditions. Hence, we suspect that the amino group is planar in both the ground and excited electronic states of AMeS.

This speculation is supported by the crystal structure, which shows two hydrogen-bound molecules per asymmetric unit (Figure 7). The acceptor molecule has the aniline ring tilted at 17° to permit the donated proton to form tetrahedral geometry about the nitrogen. The H-bonding is also accomplished by the amino assuming a pyramidal geometry in the acceptor molecule. The donor molecule, however, has a *planar* amino group and a nearly coplanar ring-ethylene-ring system. (It is likely that the deviation from coplanarity is a dynamic disorder in the crystal caused by the low-frequency, large amplitude vibrations populated at room temperature. A similar effect has been observed in crystal studies of *trans*-stilbene.¹⁶) We strongly suspect that the donor molecule geometry is closer to that of the isolated gas phase molecule. Because the acceptor must accommodate an additional atom, its structure should be more greatly perturbed.

Consideration of the aniline crystal structure strengthens these arguments. The aniline crystal also has two hydrogen-bound molecules per asymmetric unit in a geometry similar to that observed for the amino-substituted rings in AMeS.¹⁷ However, in aniline, which is known to have a pyramidal amino group in S_0 of the isolated molecule, both the acceptor and the donor have a pyramidal NH₂ geometry.

Note that, in the acceptor molecule in AMeS, the bisector of the NH_2 angle stays perpendicular to the ring, which is tilted by 17° to accommodate the hydrogen bond. This indicates that



Figure 7. Crystal structure of *trans-p-amino-p'*-methylstilbene. Top: Unit cell showing two hydrogen-bound molecules per asymmetric unit. Middle: Donor geometry with a planar amino group. Bottom: Acceptor molecule. The amino group is pyramidal to accommodate the additional hydrogen, and the aniline ring tilts by 17° to allow the correct geometry. Rotation about the C_e-Ph bond, as opposed to the N-Ph bond, indicates amino participation in the π system and a low C_e-Ph bond order in S₁.

it is energetically more favorable to rotate about the C_e-phenyl bond than about the N-phenyl bond in the ground state. This suggests partial π bonding between the amino and phenyl groups, further supporting a planar NH₂ geometry in the isolated molecule. This also supports the assertion that there is little delocalization over the ethylenic linkage in S₀, so that changes in the π system caused by amino substitution are not significantly transmitted to the methylated ring in that state.

The data provide compelling evidence that the stilbene π system is localized in S₀ and significantly more delocalized in S₁ and that the behavior of the methyl barrier correlates with changes in the π system. What remains to be discussed is the specific mechanism for the interaction between the π system and the CH₃ group. The dominant factor in barriers to methyl internal rotation is currently a topic of significant debate. Some groups subscribe to a steric interaction model, which has successfully reproduced small, 6-fold barriers in *para*-substituted molecules.⁵ A π -bonding model appears valid for aliphatic systems containing π bonds.^{18,19} Other electronic models have been developed as well.²⁰ In the remainder of the Discussion section, we will present some symmetry-based ideas and discuss their relevance to established models and the AMeS data.

If we consider possible electronic interactions between a methyl group and a molecule containing π bonds, it is convenient to consider the π -like orbitals on the CH₃ group. Two such bonding orbitals can be constructed as shown in Figure 8. Linear combinations of these orbitals are also possible. Note that the carbon p orbital makes a similar contribution to the π_{CH_3} in both cases, which indicates that the carbon does not have a significant *direct* influence on the barrier to internal rotation. If we consider this group attached to a planar molecule of the form CH₃-CH=X, we see that there is an asymmetry in the molecule's π system about the rotor axis. This simple observation leads to the conclusion that the π_{CH_3} orbital that is the most stable should also have an asymmetry with respect to each side of the molecular plane. Specifically, Hehre¹⁸ and, later, Houk, and co-workers¹⁹ have shown that a repulsive, fourelectron interaction between the π_{CX} and π_{CH_3} orbitals causes the CH₃ to reduce the overlap and assume an eclipsed conformation. Note that it is the methyl hydrogen interaction with the secondary atom, X, that is the deciding factor. The carbon p orbital in π_{CH_3} does have an *indirect* effect, in that the



Figure 8. Two degenerate π -like methyl orbitals. Orbital I has asymmetry with respect to the vertical plane and should be preferred when the π density of the parent molecule has an asymmetry in π density. Orbital II has symmetry with respect to the vertical and should be preferred in symmetric π systems such as toluene.

C-C bond order, and length, will affect the overlap between the methyl hydrogens and the secondary atom.

In aliphatic systems with an asymmetric π density on each side of the plane, the interactions are similar but more difficult to handle conceptually. First, since there are several π MOs, there are more $\pi_{CH_3}-\pi$ interactions to consider. Secondly, since each π orbital has some density on each side of the plane, there are opposing forces on the methyl that cancel to a large degree. In other words, the π density on each side of the plane contributes a 3-fold term to the potential, but the contributions from each side are 60° out of phase and tend to cancel. Nonetheless, an asymmetry in the molecular π system leads to incomplete cancellation and typically results in a 3-fold barrier and a C–H bond eclipsing the plane.

In aromatic systems where the parent molecule π MOs are symmetric on either side of the plane, the cancellation of the 3-fold terms is complete. However, the methyl group lacks true conical symmetry, so there are steric differences in the conformations that the CH₃ can assume. The methyl will adopt a conformation and orbital that reflects the symmetry of the π system. Hence, a staggered geometry will be adopted and π_{CH_2} orbital II will be favored. This results in a 6-fold barrier because there are six equivalent staggered conformations when the two sides of the planar parent molecule are identical. While it is true that this orbital has an asymmetry above and below the molecular plane, it should be remembered that the molecular π orbitals themselves are not symmetric above and below the plane. They are antisymmetric, and given the lack of true conical symmetry for the CH₃, orbital II is the closest form the $\pi_{\rm CH_3}$ can adopt to reflect the characteristics of the molecular π system. Here again, the methyl carbon p orbital contribution is essentially the same for all conformations, and it does not make a direct contribution to the barrier. However, the indirect effect of changing the steric interactions due to the differences in the C-C bond order and length is important in these systems.³

Parmenter and co-workers' ⁵ ability to accurately fit the ground and excited state methyl barriers in toluene using only steric terms strongly indicates that they are indeed dominant when the parent molecule has symmetry about the rotor axis. High-resolution studies in the microwave²¹ and UV³ regions indicate that the methyl tilts off the *para* axis due to these steric interactions. It should be pointed out that the 6-fold steric terms exist in molecules that have 3-fold barriers, but they are not dominant. An equally important thought is that in molecules with 6-fold barriers there is no *net* 3-fold term, but the forces causing them still exist and can be considered to contribute two

canceling, out-of-phase 3-fold terms that are significantly larger than the 6-fold term. Thus, small perturbations that affect the two 3-fold terms differently can spoil the cancellation and produce effects on the order of the 6-fold term. We suspect that this principle may be the cause of observed intensity in the forbidden double prime transitions in V_6 molecules.

If these ideas are applied to *para*-substituted toluenes, a low 6-fold barrier is predicted when the substituent has symmetry about the para axis. In this case, the substituent cannot cause any asymmetry in the π density between the two sides of the para axis. In cases where the substituent does not have para axis symmetry, an asymmetry in the π system can be induced and the methyl can have a 3-fold barrier. Such substituents would include hydroxy, methoxy, and ethene. However, if these substituents create only a small density difference in the carbons adjacent to the methyl-substituted position, either 6-fold or very low 3-fold barriers will result. Experimentally, low barriers (typically 6-fold) are observed for the ground and excited states of these molecules. If we consider trans-p-methylstilbene as a para-substituted toluene, we might expect similar behavior. In S₀, the barrier is $V_3 \simeq 30 \text{ cm}^{-1}$, which is 3-fold and comparable to that observed in 4-methylanisole (CH₃PhOCH₃),²² p-cresol (CH₃PhOH),²³ and *p*-methylstyrene (CH₃PhCH=CH₂).²⁴ The excited state, however, has $V_3 = 150 \text{ cm}^{-1}$, which is significantly higher than the values for the other species. This is in spite of a similarity in the HOMO and LUMO orbitals on the toluene ring. In stilbene, the remote ring has a much greater influence in the excited state due to the greater delocalization in S_1 . This increase in delocalization provides the link by which the π system of the remote ring (which is not on the *para* axis of the toluene ring) can induce asymmetry in the π system in the vicinity of the CH_3 in *p*-methylstilbene.

The conclusion that it is the remote ring that dominates the S_1 barrier, as opposed to the ethylenic bond, comes from the observation of a low S_1 barrier in *p*-methylstyrene²⁴ compared to tS. Furthermore, if the ethylenic group has the dominant influence, substitution on the remote ring would be expected to have little effect on the S_1 barrier. Here we report the opposite, a nearly 3-fold decrease in the S_1 barrier with *p*-amino substitution on the distant ring, confirming the importance of that ring to the methyl barrier.

The next issue to consider is why the barrier decreases with amino substitution. In addressing this question it is important to keep in mind that the methyl barrier is determined by the π electron density *difference* between the two *meta* carbons (β to the CH₃), not the absolute π density. Substitution on the remote ring with the strongly donating NH₂ group will do little to change the density difference in the ground state because the system is not delocalized over the ethylene linkage in that state. As a result, the AMeS and MeS barriers are quite similar for S_0 . With the delocalization that occurs in the excited state, density changes can occur in the toluene ring. With a strong substituent, such as the amino group, we would anticipate that the inherent asymmetry in the MeS excited state might be reduced, reasoning that donation to the less electron rich of the two meta carbons will occur more easily. This reduction in the π density asymmetry would cause a reduction in the methyl barrier in S_1 , which is what is observed. If this is the correct conceptual model, para substitution on the remote ring with strongly withdrawing groups should also reduce the S₁ barrier, owing to the greater difficulty in extracting density from the more electron-poor meta carbon.

Summary and Conclusions

Amino substitution at the para position of the distant ring lowers the S₁ methyl barrier in AMeS by nearly a factor of 3 compared to MeS. This dramatic effect caused by substitution 10 atoms away provides nearly conclusive evidence that π electron interactions have an important influence on methyl barriers. Molecular orbital calculations, the factor of ~ 5 increase in ring torsional frequency, the rotation of the whole aniline ring instead of just the amino group to accommodate a hydrogen bond in crystalline AMeS, and the small S₀ but large S_1 methyl barrier in MeS all indicate that the ground state π system is localized in the stilbenes, but that the excited state is significantly delocalized. Thus, the stilbene backbone has a unique ability: it enables the investigator to switch on the delocalization of the π system via excitation. Accordingly, the dramatic distant substituent effect of the strongly donating amino group on the CH₃ barrier is observed only for the S₁ state and not the ground state.

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