Structural Information from Methyl Rotors: Methyl Torsional Barriers in *p*-Hydroxy-*p*′-Methyl-*t*-Stilbene and Its Water Complexes

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The barriers to internal rotation for the methyl group in *p*-hydroxy-*p*′-methyl-*t*-stilbene and its one- and two-water complexes are reported. The jet-cooled fluorescence excitation spectra of these species are also presented. The excitation spectrum of both *p*-hydroxy-*t*-stilbene and *p*-hydroxy-*p*′-methyl-*t*-stilbene exhibits two origins separated by ∼270 cm^{-1}, which are due to the *syn* and *anti* conformers of the hydroxy group. The frequency difference between the two conformers changes dramatically in the water complexes. Additionally, barriers to internal rotation show a strong water complex dependence, changing by as much as 25% with hydrogen bonding at the hydroxy group, a site 12 atoms away from the methyl rotor.

Introduction

Several models have been proposed to account for the origin of methyl barriers, and there is currently some debate over the relative importance of steric effects vs π-electron effects.[1−4] This group has sought to demonstrate the importance of π-electron interactions by investigating distant substituent effects in *para* substituted *p*′-methyl-*t*-stilbenes.[5,6] In such systems the substituents cannot have a direct steric influence on the methyl barriers. In *p*-amino-*p*′-methylstilbene (AMeS)[5] it was found that amino substitution caused a subtle change in barrier relative to *p*-methlystilbene (MeS)[7] in the relatively localized ground state of the stilbene system. However, a 3-fold reduction of barrier was observed for the delocalized S_1 state, illustrating that the π system can be a dominant influence on the barrier to methyl internal rotation. Subsequent work on *p*-methoxy-*p*′-methylstilbene (MoMeS) showed a smaller change in S_1 barrier than AMeS, as expected, owing to the lower electron-donating capacity of the methoxy group compared to that of the amino group.[6] Additionally, two methoxy conformers were observable and the methoxy donating power was found to be dependent on its orientation. The red-shifted conformer was determined to be the stronger donor and was assigned from vibronic evidence and rotational coherence spectroscopy as the *syn* (with respect to the ethylenic linkage) conformer.[6,8] Interestingly, the subtle difference in donor strength of the methoxy group in the two conformers of MoMeS resulted in an approximately 10% difference in S_1 methyl barrier. The sensitivity of the methyl group barrier to distant and subtle changes in the parent molecule π system suggests use of the methyl barrier as a probe of electronic and molecular structure. To this end we have decided to investigate *p*-hydroxy-*p*′-methylstilbene (HMeS) and its water complexes.

Experimental Section

The jet apparatus is constructed from a 6 in. nominal six-way cross evacuated by a Varian VHS-6 diffusion pump. Samples were heated to 110−130 °C, entrained in 0.2−7 bar helium, and expanded into the vacuum using a General Valve Series 9 pulsed nozzle with a 0.8 mm diameter orifice. For the water complex work, the sample reservoir and a water reservoir were placed in parallel gas lines and a fine metering valve was used to control the water concentration. The jet was crossed at 90° by the beam from a Lumonics Hyperdye 300 dye laser (0.07 cm^{-1} resolution), which is pumped with a Lumonics HY750 Nd:YAG laser at a 20 Hz repetition rate. DCM dye was used to acquire the spectra and was frequency doubled in BBO. The emission was collected with a Melles Griot REM 014 ellipsoidal reflector and focused onto the cathode of an EMI 9813QB photomultiplier tube. The resulting signal was fed to an SRS250 boxcar integrator, digitized, and stored on a computer. Laser power was monitored by using a rhodamine 590 solution as a quantum counter and by detecting the dye emission with a photomultiplier tube. For the dispersed fluorescence experiments, the emission was once again collected with the ellipsoidal reflector and then focused onto a slit of length 100 μm of a Spex 0.5 m monochromator with a 3600 line/mm grating. The dispersed fluorescence spectra were acquired by taking an average of 10 2−6 min exposures with a Princeton Instruments liquid-nitrogen-cooled CCD detection system (1024 × 256 26 μm pixel CCD chip). This gave a linear dispersion of 0.0144 nm/pixel and a final resolution of 1.41 cm^{-1} per pixel in this wavelength region.

p′-Hydroxy-*p*-methyl-*t*-stilbene was synthesized in a dealkylation reaction from *p*′-methoxy-*p*-methyl-*t*-stilbene, which, in turn, was synthesized via a Wittig reaction[9] described previously.[6] Briefly, *p*′-methoxy-*p*-methyl-*t*-stilbene was added to 4 equiv of boron tribromide methyl sulfide in 30 mL of 1,2-dichloroethane under an atmosphere of pure nitrogen. The reaction mixture was refluxed until the starting material had disappeared. The mixture was then hydrolyzed by adding 30 mL of water and then diluting with ether. The organic phase was separated and washed with 1 M $NaHCO_3$ followed by 3 × 20 mL washings with 1 N NaOH. The combined NaOH washings were extracted into ether; the organic phase was separated and dried with $MgSO_4$, and the ether was removed via vacuum. The identity and purity of HMeS were assessed using 300 MHz proton NMR and gas chromatography.

Results and Interpretation

***p*-Hydroxy-*t*-stilbene**. Given the complications caused by the low-frequency modes of the stilbene backbone, the anharmonic methyl torsion, the possible hydroxy conformations, and possible multiple water complexes, it is prudent to first examine

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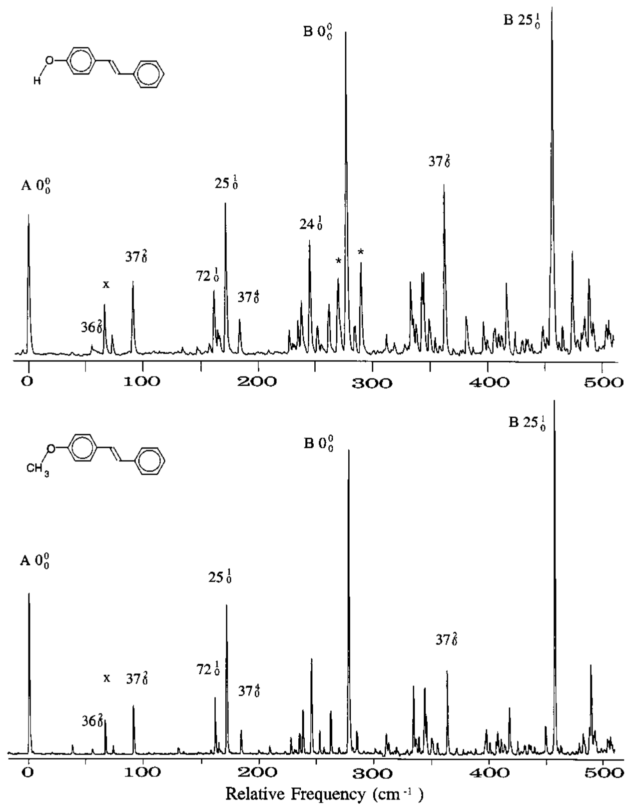

Figure 1. Fluorescence excitation spectra of *p*-hydroxy-*t*-stilbene (top) and *p*-methoxy-*t*-stilbene (bottom). A and B refer to the *syn* and *anti* coformers of the substituent, respectively. The two peaks in the hydroxy spectrum marked with asterisks are due to the one-water complex. Both absolute and relative frequencies are nearly identical for these two species. The *syn* origin is 30 517 ± 20 cm^{-1}, absolute frequency. Assignments are given in Table 1.

spectra of species simpler than HMeS + H_2O. Figure 1 shows the jet-cooled fluorescence excitation (FE) spectrum of *p*-hydroxy-*t*-stilbene (HS) and that of the previously assigned *p*-methoxy-*t*-stilbene (MoS) for comparison purposes. Immediately noticeable is the fact that these two molecules have nearly identical FE spectra in terms of both relative and absolute frequencies. For this reason, assignment of the HS spectrum by analogy to the MoS spectrum should be straightforward, including the assignment of two conformer origins as confirmed by rotational coherence spectroscopy in MoS.[8] Assignments of the stilbene normal modes are given in Table 1 following Warshel's notation[10] and are consistent with the generally agreed upon low-frequency mode assignments in stilbenes.[11 − 14] The nearly identical nature of the HS and MoS spectra indicates two other important points: (1) none of the vibronic features in the low-frequency portion of the spectrum is due to a localized functional group mode because the OH and OCH_3 mass difference would yield significantly different frequencies for such a mode and (2) changes in the stilbene mode frequencies are primarily due to the electronic influence of the substituent, which should be similar for OH and OCH_3 in the isolated molecule, rather than mass effects.

Water Complexes of *p*-Hydroxy and *p*-Methoxy-*t*-stilbene. Although the electronic effects of the methoxy and hydroxy groups on the stilbene system appear to be essentially identical, the hydrogen-bonding interactions are not. Figure 2 shows the changes in the HS and MoS spectra as a function of increased water vapor pressure. Methoxystilbene shows no evidence of complexation under expansion conditions in which the hydroxystilbene is nearly completely complexed (fourth and fifth traces of Figure 2). With large partial pressures of water the MoS finally shows some complexing at frequencies different from those observed for HS + H_2O. Under these conditions, the bare HS and HS + $1H_2O$ species show nearly complete depletion. Since both methoxy and hydroxy groups can function as proton acceptors but only hydroxy is a good donor, we would expect HS + H_2O and MoS + H_2O to behave similarly if the substituted stilbene functioned as a proton acceptor. Therefore, we interpret the dramatically different complex behavior to mean that the hydroxy group in HS donates a proton to the water molecule. This is consistent with the view that hydroxy groups attached to aromatic systems are more acidic than water[15−17] and should therefore donate a proton to the water when a complex is formed.[18−20] Because the peaks labeled A and B grow at the same rate as the two bare molecule origins deplete, we assign these transitions as two conformers of the single-water complex. It is interesting to note that the two conformer origins are much closer in frequency than for bare HS. At higher water concentrations a second pair of origins, also more closely spaced than the bare molecule's, is formed to the red. These transitions grow more rapidly as the single-water complex peaks deplete, so we tentatively assign them as the HS + $2H_2O$ conformers. At very high concentrations, new peaks can be discerned in the MoS spectrum that appear at different relative frequencies compared to HS + H_2O. These transitions are due to MoS + H_2O and are likely due to water attached to the methoxy group but may be due to a π complex. These issues will be further addressed in the discussion section.

***p*-Hydroxy-*p*′-methyl-*t*-stilbene**. The *p*-hydroxy-*p*′-methyl-*t*-stilbene (HMeS) fluorescence excitation spectrum is shown in Figure 3 along with *p*-methoxy-*p*′-methyl-*t*-stilbene (MoMeS) for comparison. We were unable to completely dry the HMeS, so some water complex peaks are visible in the FE spectrum (the origins are marked). With the exception of the water complex transitions, the spectra of HMeS and MoMeS are nearly

TABLE 1: Band Displacements (from 0^0_0 $0a_1$, in cm^{-1}) for Transisitons Involving Stilbene-like Normal Modes in the Hydroxy Stilbenes

	p-hydroxystilbene		*p*-hydroxystilbene + H_2O		*p*-hydroxy-*p*-methylstilbene		*p*-hydroxy-*p*-methylstilbene + H_2O	
transition	*syn*	*anti*	A	B	*syn*	*anti*	A	B
36^2_0	55.5	60			59.4	52		
37^2_0	91.5	85	92	91				
$36^1_0 37^1_0$	73.5	72						
x	67	67						
25^1_0	171	179.5	185	184	159	167	174.4	173
37^4_0	183.8	171.0	180	179				
24^1_0	245.3	211	263	262	230	203	243	243
25^2_0	342.5	358	368	367	318	334	348	347
$25^1_0 24^1_0$	416.5	390			389	636	416	415
25^3_0	516.4	537.5			476	767		
72^1_0			195	194	154	169		

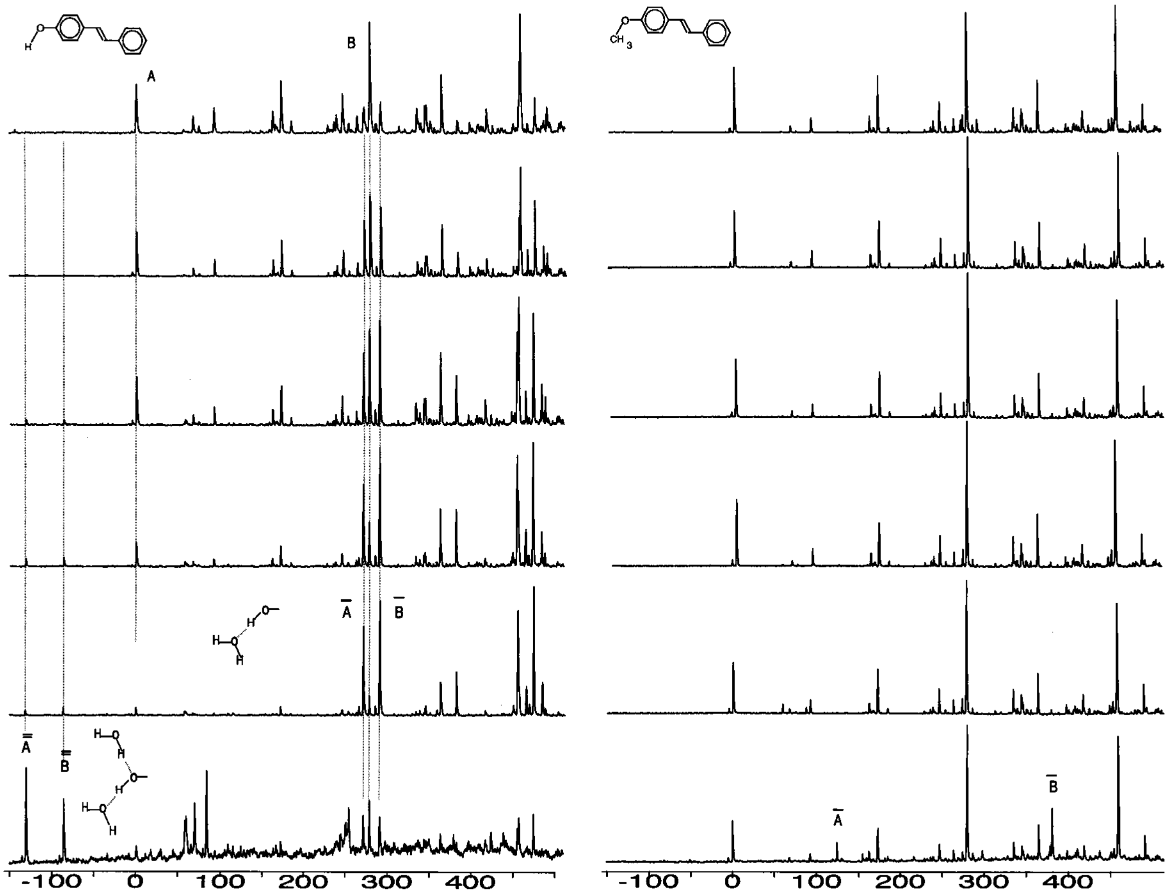

Figure 2. Effect of added partial pressures of water on the hydroxy and methoxy stilbene spectra. Water concentration increases from top to bottom. A and B denote the *syn* and *anti* conformers of the hydroxy or methoxy group. Single and double bars over the A and B denote the one- and two-water complexes, respectively. Note the growth of the two peaks below 300 cm^{-1} as the bare molecule origins deplete. Also, note the formation of the two-water complex in the bottom spectrum. *p*-Methoxy-*t*-stilbene only begins to show water complexes at the very high concentrations where *p*-hydroxy-*t*-stilbene forms a two-water complex.

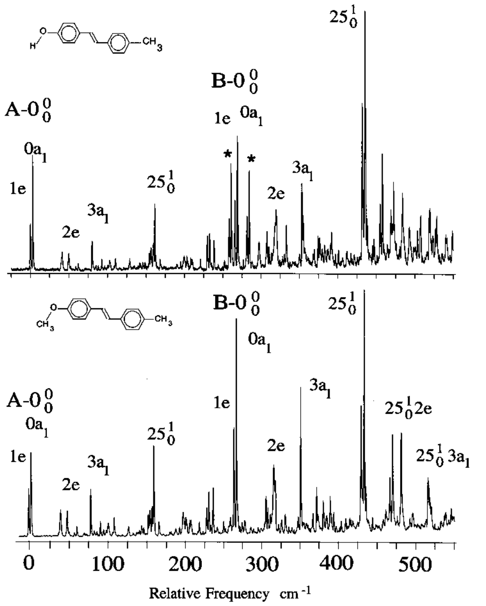

Figure 3. Fluorescence excitation spectra of *p*-hydroxy-*p*′-methyl-*t*-stilbene (top) *p*-methoxy-*p*′-methylstilbene (bottom). With the exception of water complex peaks, which appear as doublets on each side of the B (*anti*) origin (marked with an asterisk), the two spectra are nearly identical as is seen for the unmethylated molecules. Torsional frequency assignments are given on the spectrum and in Tables 1 and 2.

identical with each other, consistent with the similarity observed for the unmethylated parent molecules MoS and HS. This is true for the methyl torsional transitions, labeled 0a, 1e, 2e, 3a, and 4e, as well. Fits of the torsional frequencies using a particle-in-a-ring basis set perturbed by a $^1/_2V_3\ [1 - \cos 3\varphi]$ barrier reveal that the torsional barriers are essentially identical for the corresponding conformers of HMeS and MoMeS. However, the two conformers for each species have barriers that differ by about 10%, 92 and 104 cm^{-1} for the red and blue conformers, respectively.

When low partial pressures of water were added to the expansion, HMeS readily formed complexes with origins at relative frequencies similar to those observed in HS + H_2O. MoMeS did not easily form complexes. The FE spectrum for HMeS + H_2O is shown in Figure 4. Again, the two complex origins have shifted much closer in frequency with the addition of water. The complex also displays different methyl torsional frequencies compared to the bare molecule, and fits of these frequencies yield barriers of 78 and 74 cm^{-1} for the red and blue conformers, respectively. The complex shows a significant reduction in barrier and a reduction in the conformer barrier *difference* compared to the bare molecule.

The pair of red-shifted complex origins, tentatively assigned as HMeS + $2H_2O$, is shown in Figure 5. These transitions are also at a similar relative frequency to the red complex transitions observed in the hydroxystilbene plus water spectrum. Fits of the labeled methyl torsional transitions yield barriers of 96 and 98 cm^{-1}, respectively, for the low- and high-frequency conformers (Tables 2 and 3). These barriers are nearly the average of the two conformer barriers for the bare molecule (92 and 104 cm^{-1}), and the conformer barrier *difference* is again significantly reduced for this complex.

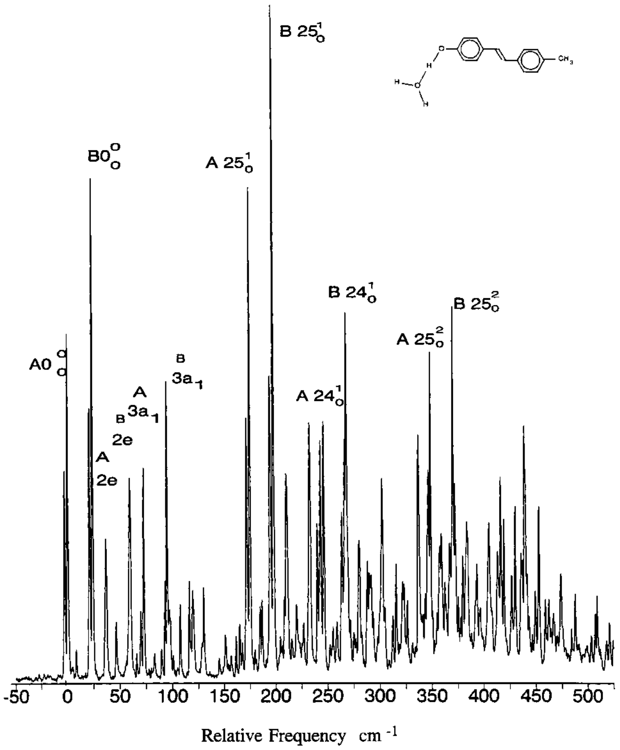

Figure 4. Excitation spectrum of *p*-hydroxy-*p*′-methyl-*t*-stilbene plus water. Because we get nearly complete complexation, all labeled transitions, and virtually all transitions of appreciable intensity, are due to the single-water complex. Note the reduction in frequency difference for the *syn* and *anti* conformers, from approximately 270 cm^{-1} in the bare molecule to approximately 25 cm^{-1} in the water complex. Torsional transition assignments are given in the spectrum and in Tables 1 and 2.

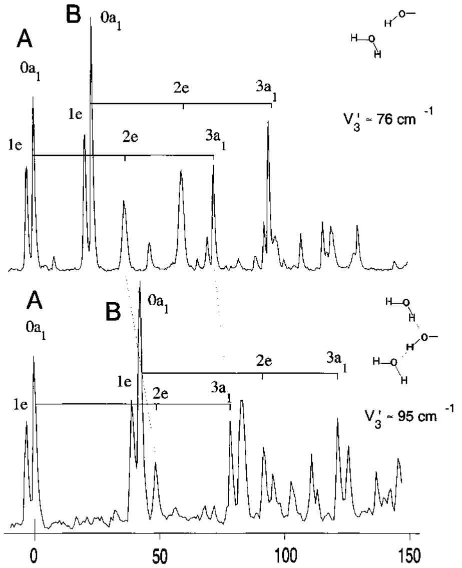

Figure 5. Low-frequency portion of the excitation spectrum for the one- and two-water complexes of *p*-hydroxy-*p*′-methyl-*t*-stilbene showing the methyl torsional assignments. A and B denote the *syn* and *anti* conformers of the hydroxy group for each complexed species. Because of the high conversion to the complex and the frequency offset for the different complexes (as seen in Figure 2), virtually all transitions in each spectrum are due to the species indicated. Fits for these transitions are presented in the tables.

TABLE 2: Experimental Methyl Torsional Band Displacements (from 0^0_0 $0a_1$, in cm^{-1}) for *p*′-Hydroxy-*p*-methyl-*t*-stilbene Conformers and Water Complexes in the S_1 Excited State and Barrier Terms (in cm^{-1}) That Yield the Best Fit to the Data

	hydroxymethyl		hydroxymethyl·(H$_2$O)$_1$		hydroxymethyl·H$_2$O)$_2$	
	A	B	A	B	A	B
band						
$0a_1$	0	0	0	0	0	0
1e	−3.0	−3.3	−2.8	−2.9	−3.0	−3.1
2e	47.0	51.0	39.2	38.1	49.55	50.2
$3a_1$	77.3	84.5	72.4	70.8	80.25	80.2
4e			99.6	98.5		
barrier term						
V_3'	91.26	103.9	77.8	74.5	96.4	97.8
V_6'	16.10	10.49	−9.9	−9.0	15.1	21.3

TABLE 3: Calculated Methyl Torsional Band Displacements (from 0^0_0 $0a_1$, in cm^{-1}) for *p*′-Hydroxy-*p*-methyl-*t*-stilbene Conformers and Water Complexes in the S_1 Excited State and Barrier Terms (in cm^{-1}) That Yield the Best Fit to the Data

	hydroxymethyl		hydroxymethyl·(H$_2$O)$_1$		hydroxymethyl·(H$_2$O)$_2$	
	A	B	A	B	A	B
transition						
$0a_1$	0	0	0	0	0	0
1e	−3.0	−3.3	−2.39	−2.02	−3.0	−3.1
2e	47.08	51.04	39.2	38.12	49.0	51.0
$3a_1$	77.19	84.49	72.4	70.82	80.20	80.8
4e			100.8	98.45		
barrier terms						
V_3'	91.26	103.9	77.8	74.5	96.4	97.8
V_6'	16.10	10.49	−9.9	−9.0	15.1	21.3

Discussion

Previous work on *p*-amino and *p*-methoxy substituted *p*′-methylstilbenes has shown that electron-donating groups in the *para* position on the distant ring reduce the S_1 barrier to methyl internal rotation.[5−7] This has been explained in terms of a π-electron interaction model similar to that of Hehre and Houk.[1,2,6] A π-like orbital on the methyl group interacts with the π system of the parent molecule. If the π density is symmetric with respect to the rotor axis, a small 6-fold barrier results. If the π density is asymmetric, a 3-fold barrier results and the greater the asymmetry the larger the barrier. In MeS, the ground state has a low 3-fold barrier because the π system is not very delocalized, so the central double bond and distant ring have a small influence on the CH$_3$-substituted ring. Conversely, the excited state, which is known to have greater delocalization,[10, 11] displays a CH$_3$ barrier that is 5 times greater. This higher barrier is caused by a greater asymmetry about the rotor axis, which, in the Hehre model, would indicate a π density difference in the two positions adjacent to the methyl group. Semiempirical calculations do predict a density difference and a slight increase in that difference in the excited state, but the magnitude of the change is not consistent with experimental results. Substitution in the *para* position on the remote ring with an electron donor will cause a π-density increase in both positions adjacent to the CH$_3$ but should cause a greater increase in the position that was originally more electropositive. This will reduce the *difference* in density and cause a lower barrier as was observed. In MoS, it was found that the electron-donating strength of the methoxy group was dependent on its conformation.[6] The S_1 methyl barrier was lower for the better donating conformer in MoMeS, consistent with the above model.

HS and HMeS should, and do, act in a fashion very similar to the behavior of analogous methoxy stilbenes, so their behavior is really explained by the previous work. What remains to be examined is whether the behavior of the water complexes is consistent with the existing model.

We will first consider HS + H_2O. The most notable change in the complex spectrum, compared to the bare molecule, is the drastic reduction in frequency difference between the two conformer origins. Because the HS and MoS spectra are nearly identical, we know that it is the lone pair position that dominates the relative energetics of the two conformers. We can also surmise, from the different behavior of HS + H_2O and MoS + H_2O, that the hydroxy group donates a proton to the water in the complex.

In the limiting case of complete proton donation to the water, the charge density on the oxygen would increase and become symmetric about the *para* axis. In this case there would no longer be two conformers, so there would not be two origins or a conformational energy difference. Short of this limiting case, partial donation of the hydroxy proton will both increase the charge density on the oxygen ***and*** make the density more symmetric with respect to the *para* axis. Since it is the lone pair (or electron density) that primarily determines the conformational energy difference, a more symmetric distribution will reduce the energy difference and will bring the origins closer in frequency. Proton donation by the hydroxy will also increase the overall density at the oxygen, making OH + H_2O a better electron-donating group than OH alone. This is evidenced by an increase in the ring torsional (37^2_0) frequency with the addition of water, particularly for the blue conformer (Table 1). We know that better electron donors in the *para* position on the distant ring reduce the S_1 methyl barrier in substituted *p*′-methylstilbene. Thus, if the above model is correct, we would expect complex formation to reduce the methyl barrier if the hydroxy group acts as a proton donor. In fact, an approximate 20% reduction is observed (Tables 2 and 3), consistent with the model.

Now we will consider the second (red-shifted) water complex. Possibilities for the structure of this complex include a second water hydrogen bonding to the π system, two waters bound at the OH site, or a single water at a different site. As stated in the Results and Interpretation section, these transitions only become dominant at higher water concentrations and when the single-water complex shows signs of depletion. For this reason we assign the red-shifted complexes to HS + $2H_2O$. Sakalley and co-workers[21] have shown via high-resolution IR spectroscopy in a jet that the water trimer structure is likely a six-membered ring with each water acting as both a proton donor and a proton acceptor. Since the hydroxy group can function in the same manner, we speculate that a similar structure is formed in HS + $2H_2O$.

If this is the correct structure, let us consider what would be expected for conformer energy differences and methyl barrier changes in HMeS. If the hydroxy group is donating a proton to one water and accepting a proton from a second water, the hydroxy oxygen will have a partial bond to a hydrogen on both sides of the *para* axis. This should lead to a more symmetric charge density, which reduces the conformer energy *difference*. Additionally, the effects of an electron density increase at the oxygen caused by proton donation and a density decrease caused by accepting a proton should approximately cancel. Thus, we expect OH + $2H_2O$ to be a comparable electron-donating group to OH and we would expect similar S_1 methyl **barriers** in HMeS and HMeS + $2H_2O$ but a smaller *barrier difference* between the two conformers of the $2H_2O$ complex compared to the barrier difference between the two bare molecule conformers. This is what is observed. For HMeS + $2H_2O$, the two conformers have barriers that differ only by 2% (96 and 98 cm^{-1}) and are nearly the average values of the two HMeS conformer barriers (91 and 104 cm^{-1}), which have a greater than 12% barrier difference.

Note that for both HMeS + H_2O and HMeS + $2H_2O$, the electron-donating properties of the two conformers are made more similar (compared to the bare molecule) by complex formation. Accordingly, the *difference* in the methyl barriers between the *syn* and *anti* hydroxy conformers is reduced for the water complexes.

Ring Torsional Surface. In MoS we observed a fairly strong transition at 67 cm^{-1}, which had no analogue in stilbene or *para* substituted stilbenes with substituents that have *para* axis symmetry. The same transition is observed at the same frequency in HS, which rules out a functional group made of the substituent because the mass difference between OH and OCH_3 would result in a significant frequency difference. In MoS we tentatively assigned the transition as a newly allowed phenyl torsional level caused by symmetry lowering of the ring torsional surface. In *t*-stilbene, the ring torsional surface has four equivalent minima with pairs of minima originating from the 2-fold symmetry of each ring. In MoS or HS, the substituent conformations have significant energy differences and flipping the substituted ring will result in conversion between the energetically different conformers. This modifies the ring torsional surface from the four equivalent minima in *t*-stilbene to two pairs of equivalent minima with the pairs differing in energy by ~270 cm^{-1}. In HS, compared to MoS, we have the ability to further modify the surface by adjusting the conformer energetics via water complex formation. In HS + H_2O we know that the energy difference between the two conformers is greatly reduced compared to those of HS and MoS. There is still symmetry lowering of the surface compared to *t*-stilbene, but it is not as large an effect as seen in HS and MoS, so we would expect a change in this transition. The HS + H_2O spectrum does display some transitions in this low-frequency region that cannot be assigned as known transitions in *t*-stilbene, but they are much less intense than the 67 cm^{-1} transition observed in the bare molecule. This result is consistent with the assignment of the 67 cm^{-1} peak in MoS as a ring torsion newly allowed for symmetry lowering.

Complex Shifts. One of the puzzling issues in the water complex spectra is the blue shift observed when the hydroxy group acts as a proton donor. Red shifts are observed in most phenols in this case.[18,20,22] Although our observation seems to run counter to previously observed proton donor/acceptor shifts, we are confident of our assignment for several reasons. (1) HS is a better acid than water and thus should be the proton donor. (2) HS and MoS show completely different water complex behavior. If they both functioned as proton acceptors, we would expect similar behavior. Since only HS can function as a donor, donation would account for the different behavior, particularly the fact that HS forms complexes much more easily than MoS. (3) The HMeS + H_2O methyl barrier behaves as predicted if the hydroxy group is the proton donor.

Although we are confident of our assignment, we are unable to develop a consistent explanation for the complex shifts that occur. It is worth noting that He complexes of all the stilbenes we have investigated show a *red* shift, which is opposite to the blue shift observed in most molecules. We suspect the large increase in delocalization that occurs in excitation to S_1 plays a role in the complex shift behavior of the stilbenes.

Summary and Conclusions

Previous work on *para* substituted *p*′-methyl-*t*-stilbenes has shown that the methyl group is a sensitive probe of the local π-electron environment and of any changes to that environment caused by substitution at a distant site. This work, along with the MoS and MoMeS work, shows that subtle changes in the π system caused by substituent conformation or complexation can lead to 10−20% changes in barriers for a methyl group 10 atoms away. Furthermore, the changes in the CH_3 barrier can be interpreted to help give structural information about the complexes.

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