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ARTICLES

Theoretical Study of Solvent Effects on the Intramolecular Charge Transfer of a Hemicyanine Dye

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4-[2-(4-Dimethylaminophenyl)ethenyl]-1-methylpyridinium iodide (HR) is a solvatochromic dye and is widely used in Langmuir−Blodgett (LB) film preparations. Quantum chemical calculations combined with a cylindrical solvation model are used to investigate the possibility of TICT (twisted intramolecular charge transfer) state formation by rotating part of the molecule around several different chemical bonds. The results account for most of the experimental observations and partially confirm the assumption that the structure of HR is a compromise between benzenoid and quinoid resonance forms. It is revealed that the TICT state can be formed by rotating the dimethylamino group to the perpendicular position in polar solvents. But this probability should be very small due to the relatively high energy barrier to the rotation in the excited state. Rotations of the pyridyl ring and the aniline ring enhance the charge transfer in the first excited state. There is a small energy barrier to the rotation of the pyridyl ring in the first excited state. In polar solvents, there is no barrier to rotation of the aniline ring in the excited state. The high-energy barrier to rotation around the central double bond is the cause of the low photoisomerization yield of HR.

1. Introduction

Aromatic systems with strong electron donor and acceptor substituent groups often exhibit solvent-dependent emission properties due to internal charge transfer processes in the excited states. One of the extensively studied examples is the dual fluorescence of the dimethylaminobenzonitrile (DMABN) molecule.[1−8] It is now well established that the red-shifted emission band of DMABN in polar solvents is due to the formation of the twisted intramolecular charge transfer (TICT) state which is usually characterized by enhanced or reversed charge transfer associated with rotation around a chemical bond.[9] The TICT state in DMABN is formed by rotation of the dimethylamino group to the perpendicular conformation.

4-[2-(4-Dimethylaminophenyl)ethenyl]-1-methylpyridinium iodide (HR) is one of the most widely used species in Langmuir−Blodgett (LB) film preparations.[10,11] This molecule has the electron donor $-N(CH_3)_2$ on one end and the electron acceptor methylpyridinium on the other end (Figure 1). If long alkyl chains are attached to either side, the resulting ambiphilic molecules are suitable for constructing LB films. Because of its large second hyperpolarizability β and other interesting features, HR has gained much attention in nonlinear optical research and molecular electronics.[10−13] Since there is an electron donor and an electron acceptor in the same molecule, intramolecular charge transfer is expected when the molecule is excited. Unlike the well-studied TICT species DMABN, the existence of a TICT state in HR has not been confirmed since it does not have the typical dual fluorescence.[14] The wavelength of the observed emission is not very sensitive to solvent polarity. Table 1 lists the absorption and fluorescence maxima, and the fluorescence and photoisomerization yield of HR in different solvents. The maximum of the absorption spectrum of HR shifts to the blue and the fluorescence yield decreases in more polar solvents. This is in contrast to most TICT state compounds,

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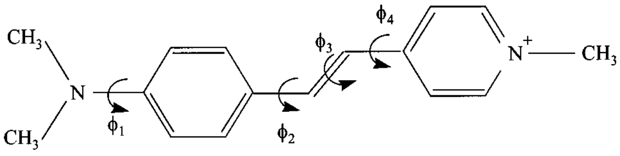

Figure 1. Chemical structure of 4-[2-(4-dimethylaminophenyl)ethenyl]-1-methylpyridinium (HR) in the trans conformation. ϕ_1, ϕ_2, ϕ_3, and ϕ_4 indicate four possible rotations inside the molecule.

where both absorption and fluorescence maxima shift to the red in polar solvents. This suggests that fluorescence originates from a non-TICT state and that TICT state formation lowers Φ_f. Additionally, HR has a larger absorption spectral line width in more polar solvents (Table 1). The line width of the absorption spectrum of HR in aqueous solution is considerably larger than in organic solvents.

HR has been studied by surface-enhanced Raman spectroscopy[15] and resonance Raman spectroscopy,[16] and a resonance between the benzenoid and the quinoid forms has been assumed (Figure 2). In studying the spectra of stilbene-like derivatives,[17,18] Tsukada et al. used the theory of two resonance forms to explain the shift of the vibrational frequencies of the central double bond and the single bonds connecting the ethylene group when these molecules are in different environments. It is believed that in more polar solvents, the benzenoid form makes a larger contribution, while in nonpolar solvents, the quinoid form dominates since the benzenoid form has more localized π-electrons than the quinoid form. The resonance structure of HR was also used to explain the shift of λ_{abs} to the blue in more polar solvents.[15]

In studying the fluorescence of the compounds that are similar in structure to HR, Fromherz et al. invoked the TICT state to explain the fluorescence of these compounds in different solvents.[19] They also studied the fluorescence of some other pyridinium compounds in which rotation of the aniline group is involved. Their results suggested that the TICT state could be formed by rotation of the aniline group.[20,21] Since there are several chemical bonds in HR that may be involved in rotation, TICT states might form by twisting around one or more of these bonds. Recently, Rettig et al. calculated the spectroscopic properties of HR using the semiempirical CNDO/S method,[9] performed as a function of rotation about various chemical bonds. Their work suggested that there are several competing TICT channels when the HR molecule is excited,[9,22] but solvent effects on these channels were not considered. In this paper, we use quantum chemical calculations combined with an appropriate solvation model to investigate possible TICT states that might be formed by twisting around some of the chemical bonds in the molecule.

2. Calculation Details

2.1. Molecular Geometries. The ground-state geometry of HR may be either trans or cis conformation. The geometries were optimized with GAMESS,[23] using the AM1 Hamiltonian. Since there are two possible isomers, we optimized the geometries in both the trans and cis configurations. In the lower energy trans optimized geometry, the phenyl and pyridyl rings and the ethylene part are all in the same plane. In the cis optimized geometry, there is about 10° relative rotation of the phenyl ring and the pyridyl ring around the central double bond. The geometries of other conformations including intramolecular rotations were obtained by starting from the optimized trans geometry and rotating part of the molecule using HyperChem.[24] When rotating around a chemical bond, the rest of the molecule was kept relatively fixed. The effects of allowing the rest of the molecule to relax are considered in section 3.7. In the rotation around the central double bond, because of the repulsion force of hydrogen atoms, the geometries near the cis configuration were obtained by rotating part of the molecule starting from the optimized cis geometry, to avoid the hydrogen atom repulsions. The angles for rotation about various bonds are defined in Figure 1.

2.2. Electronic Properties. To calculate both ground and excited-state properties, two different computational approaches were combined. First the ground-state properties were calculated using GAMESS and the AM1 Hamiltonian. Then the excited-state energies were calculated using the semiempirical INDO/S[25,26] method including configuration interaction (CI). The CI calculation in INDO/S included singly excited configurations from the 10 highest occupied orbitals into the 10 lowest virtual orbitals. We found that including more singly excited configurations in the calculation had little effect on the excited-state energies. The excited-state energies were then taken relative to the ground-state energies from the AM1 calculation. Charge distributions over the atoms were used to calculate the solvation energy of the molecules using the model shown in the next section. The energy of the molecule in excited state i is

$$E_i = (E_i - E_0)_{\text{INDO/S}} + (E_0)_{\text{AM1}} + E_{\text{sol}} \qquad (1)$$

where the first term is the energy interval between the excited state i and the ground state obtained from the INDO/S calculation, the second term is the ground-state energy obtained from the AM1 calculation, and the last term is the solvation energy.

2.3. Solvation Models of Arbitrary Charge Distributions. Several approaches for incorporating solvation energies in quantum chemical calculations have appeared in the literature.[27] Hawkins et al.[28] employed a generalized Born approximation and AM1 calculations to model solvation energies. Zerner and co-workers[29−31] used quantum mechanically derived solute charge distributions to compute the reaction field. Zeng et al.[32,33] employed a combination of quantum mechanical calculations and computer simulations to include microscopic solvation effects. Thompson[34−36] developed a consistent model for solute/solvent polarization in which quantum mechanical and molecular mechanics are combined to account for solvation effects. In this work, the cylindrical solvation model[37,38] is used due to the fact that HR is an elongated molecule. The coaxial cylindrical system consists of three regions, which include an inner solute region, a local region, and an outer solvent region. The electrostatic Helmholtz free energy of an arbitrary charge distribution is given by

$$A_{\text{el}} = \frac{1}{2}\sum_{\nu=1}^{p} q_\nu \phi_{\text{R}}(r_\nu) \qquad (2)$$

where the sum is over the number of charged sites; ϕ_R is the reaction potential at the charged site ν which has charge q_ν and whose position is defined by r_ν relative to the coordinate origin. If one imposes the boundary conditions and solves the Laplace equations for the three regions to get the reaction potential (ϕ_R), one will get the electrostatic free energy A_{el}. The working equations for the cylindrical cavity model have been derived by Jararam and Beveridge.[38] The cylindrical model has been successfully used to explain the relative stability of different forms of DNA.[38] Like other solvation models, the problem with

TABLE 1: Some Experimental Results for HR: Absorption Maxima (λ_{abs}), Fluorescence Maxima[14] (λ_{fluo}), Fluorescence Quantum Yield[14] (Φ_f), Trans−Cis Photoisomerization Quantum Yield[14] ($\Phi_{t\to c}$) and Full Width at Half-Height (fwhh) of the Absorption Spectra in Some Organic Solvents and Aqueous Solution

solvent	ϵ^a	λ_{abs} (nm)	λ_{fluo} (nm)	Φ_f^b	$\Phi_{t\to c}^b$	fwhh (cm^{-1})
CH_2Cl_2	8.9	512	611	0.02	≤0.01	
ethanol	24.5	475	612	0.006		3888
methanol	32.7	473			<0.002	4242
dimethylformamide	36.7	466	614	0.003	<0.005	
acetonitrile	37.5	469	614	0.001	<0.005	4278
sulpholane	43.3	474			<0.002	
H_2O	78.4	445	615	<0.001	<0.001	6014

[a] Solvent dielectric constant. [b] Excitation wavelength, λ_{exc} = 438 nm.

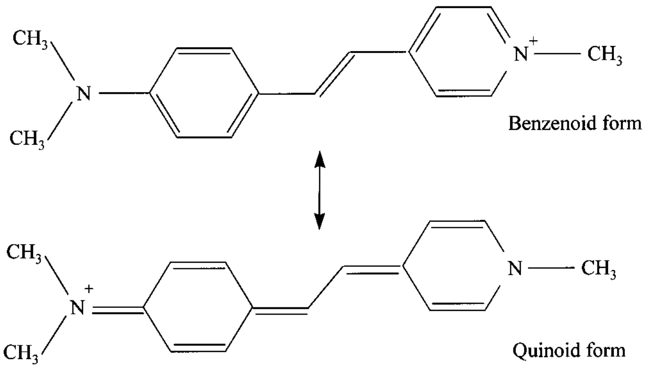

Figure 2. Two resonance structures of HR: benzenoid form and quinoid form.

TABLE 2: Mulliken Charge Distributions of HR in the Ground State (S_0) and the First Two Excited Singlet States (S_1, S_2) in the Franck−Condon Geometry

group	S_0	S_1	S_2
$N(CH_3)_2$	0.101	0.269	0.219
aniline ring	0.136	0.422	0.484
double bond	0.050	0.003	0.312
pyridyl ring + CH_3	0.714	0.306	−0.012

this model is that there are several adjustable parameters which are difficult to choose. In our calculation, the length of the cylinder was taken to be the distance between the two most distant atoms, and the radius of the cylinder was taken as the largest distance of the atoms relative to the long inertial axis. Following ref 38, the dielectric constants of the outermost shell and the second shell are taken as the bulk solvent dielectric constant and one-fourth of that, respectively. The dielectric constant of the inner solute region is fixed as 1.

3. Results and Discussion

3.1. Properties of the Gas-Phase Molecule. Starting from the trans conformation, the optimized geometry of HR obtained from the AM1 calculation results in the aniline ring and the pyridyl ring, the ethylene and the dimethylamino group being in the same plane. INDO/S calculations of the vertical electronic transitions show that the transition with the largest oscillator strength is that from the ground state (S_0) to the first excited singlet state (S_1), at the wavelength 452 nm. This transition is polarized along the long molecular axis. Table 2 summarizes the distribution of the net positive charge in the ground state (S_0) and the first two excited singlet states (S_1, S_2) for the planar conformation in the gas phase, where the molecule has been divided into four regions and the charges are summed over the atoms in each region. In the ground state, the positive charge is concentrated on the pyridyl ring, while the first singlet state is a charge transfer state with the positive charge more evenly distributed over the whole molecular system. Positive charge is transferred from the pyridyl ring to the dimethylamino group and the aniline ring. The second singlet state is also a charge transfer state, but the oscillator strength from S_0 to S_2 is very small.

The calculated energy barriers for rotations around different chemical bonds in HR in the S_0 and S_1 states are listed in Table 3 for a range of solvent dielectric constants. In the model depicted in Figure 2, increasing weight of the quinoid resonance form should lead to a higher barrier for the rotations ϕ_1, ϕ_2, and ϕ_4, while greater contributions of the benzenoid form increases the barrier to the ϕ_3 rotation. However, steric effects and solvent interactions also influence the barrier to rotation. From Table 3, in the gas phase, the rotations around the central double bond and the single bonds connecting the ethylene group and the aniline or pyridyl ring have an energy barrier of 0.0485 and 0.0130 hartree, respectively. These are much higher than room-temperature energy, which is about 0.001 hartree. So, at room temperature in the ground state, HR is in a stable trans form. Rotation in the S_1 state has totally different features, which are discussed in more detail below.

The effect of solvent on the energy barrier for rotation around different chemical bonds in the ground and excited states relative

TABLE 3: Effect of the Solvent Polarity on the Energy Barrier (in hartree, 1 hartree = 2625.5 kJ/mol) for Rotation around Different Chemical Bonds in the S_0 and S_1 States and the Energy Difference between These Two States in the Planar Geometry ($E_{S_1} - E_{S_0}$). ϕ_1, ϕ_2, ϕ_3, and ϕ_4 Represent Rotations in Figure 1. The Number in Parentheses Indicates the Position of the Energy Barrier Except As Annotated for the Gas-Phase Molecule (ϵ = 1)

		ϕ_1		ϕ_2		ϕ_3		ϕ_4	
ϵ^a	$E_{S_1} - E_{S_0}{}^b$	S_0 (90°)	S_1 (90°)	S_0 (90°)	S_1 (NA)	S_0 (90°)	S_1 (60°)	S_0 (90°)	S_1 (50°)
1	0.1006	0.0189	0.0334^c	0.0130	0.0045^d	0.0485	0.0096	0.0130	0.0015
5	0.1016	0.0201	0.0296	0.0093	0	0.0523	0.0126	0.0074	0.0025
10	0.1017	0.0202	0.0171	0.0093	0	0.0525	0.0127	0.0071	0.0025
20	0.1019	0.0205	0.0168	0.0082	0	0.0534	0.0134	0.0057	0.0028
40	0.1022	0.0207	0.0148	0.0073	0	0.0541	0.0140	0.0045	0.0030
78	0.1024	0.0208	0.0138	0.0068	0	0.0544	0.0143	0.0040	0.0030

[a] Solvent dielectric constant, ϵ = 1 for gas-phase molecule. [b] Energy difference between the S_0 and S_1 states in the planar geometry (hartree). [c] Energy barrier is at 90° for gas-phase molecule. [d] Energy barrier is at 70° for gas-phase molecule. In solution, there is no barrier to rotation ϕ_2 in the S_1 state.

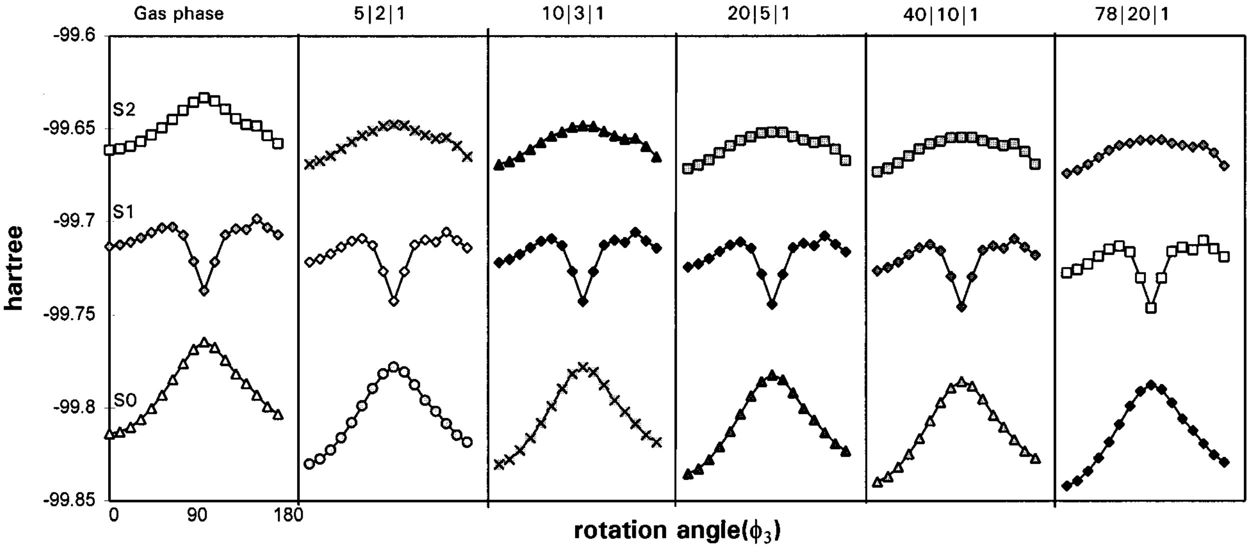

Figure 3. Energy of the S_0, S_1, and S_2 states of HR as a function of rotation about the central double bond for different solvent dielectric constants as indicated on the top of each graph. The number *a*|b|*c* on the top of each graph means the following: *a* is the bulk solvent dielectric constant, *b* is the dielectric constant of the subshell, and *c* is the dielectric constant of the inner solute shell.

to the trans planar form in the Franck–Condon (FC) region is shown in Table 3 and discussed further below.

3.2. Rotation about the Central Double Bond: Trans–Cis Isomerization. Figure 3 shows the energy changes of the ground state and the first two excited states as a function of rotation around the central double bond (ϕ_3 in Figure 1) and for a variety of different solvent dielectric constants. The numerical values of the barriers to rotation are listed in Table 3 where rotation is ϕ_3.

From Figure 3, we can see that, in the gas phase, the trans form is more stable than the cis form by 0.01 hartree. The energy barrier hindering the internal rotation (ϕ_3) in the ground state is 0.0485 hartree. This explains the thermal stability of trans HR at room temperature.[14] Figure 3 shows how the solvation effects are increased by increasing the dielectric constant of the bulk solvent. The ground-state barrier to trans–cis isomerization is higher in more polar solvents (see Table 3). This means that in more polar solvents the rotation about the central double bond is more difficult. This supports the assumption that in more polar solvents the benzenoid form dominates over the quinoid form.[15]

When the molecule is excited to the S_1 state, there is a local energy minimum at the FC geometry for ϕ_3. Since the barrier to twisting in the S_1 state is greater than 25 kJ/mol, it is concluded that HR should not undergo isomerization easily when exposed to light. This is consistent with the experimental results in Table 1, where the trans–cis quantum yield $\Phi_{t\rightarrow c}$ obtained by Görner et al.[14] using 438 nm excitation is less than 0.01 in most solvents. In contrast, other stilbene-like molecules have been observed to undergo isomerization when exposed to room light.[39] In HR, increasing the solvent polarity increases the barrier height in S_1 from 0.0096 hartree when $\epsilon = 1$ to 0.0143 hartree when $\epsilon = 78$. This reveals the fact that in the excited state the central double bond is stronger in more polar solvents. So it is more difficult for the molecule to undergo isomerization in more polar solvents. This is consistent with the general trend in Table 1. In agreement with the current theoretical model of olefin isomerization,[40,41] the potential energy curves of the ground state and S_1 state suggest that there is a strong avoided crossing, along the trans-to-cis conversion, and the configurational mixing pushes apart the two diabatic states.[5]

If molecules could be excited to high enough vibrational states within the excited-state torsional potential, then trans–cis photoisomerization would be expected to take place readily. However, the potential curves in Figure 3 suggest that there is little Franck–Condon activity of the vibration associated with twisting about the C=C bond. Coupling of the torsional vibration to other Franck–Condon active modes may explain the small observed quantum yields for photoisomerization.

Figure 4 shows how the charge distribution in the molecule changes when the molecule is rotated around the central double bond. There is charge transfer character in the perpendicular conformation of the ground state. But from the previous discussion, it's unlikely for the ground state to achieve the perpendicular conformation at room temperature. When the molecule is first excited, there is a charge rearrangement, and the positive charge is now mainly on the aniline ring. If the excited molecule can overcome the energy barrier to the perpendicular conformation, the positive charge will be more localized on the pyridyl ring. In this state if the excited molecule makes a vertical transition to the ground state, the positive charge will tend to localize on the aniline ring. This means that during this course the molecule passes through a charge transfer state before isomerizing to either the trans or cis conformation. The same observation about 4-(dimethylamino)-4′-cyano-stilbene (DCS) has been mentioned by Rettig.[22]

3.3. Rotation around the $C-N(CH_3)_2$ Bond. Rotation around the $C-N(CH_3)_2$ bond plays a major role in the TICT state formation in DMABN.[1–8,22,42] The energy curve for rotation around the $C-N(CH_3)_2$ bond in HR presents some interesting features (Figure 5).

In the ground state, the stable conformation in either the trans or the cis form has the dimethylamino group in the same molecular plane as the rest of the conjugated system. Rotation about the $C-N(CH_3)_2$ bond is greatly hindered by the high rotational energy barrier (0.0189 hartree in the ground state, gas phase). In more polar solvents, this energy barrier is further increased to 0.0208 hartree when $\epsilon = 78$. This suggests that rotation about the C–N bond is more difficult in more polar solvents. This contradicts the assumption of the two resonance form theory, which says that in more polar solvents the benzenoid form should dominate and rotation about the C–N bond should be easier.

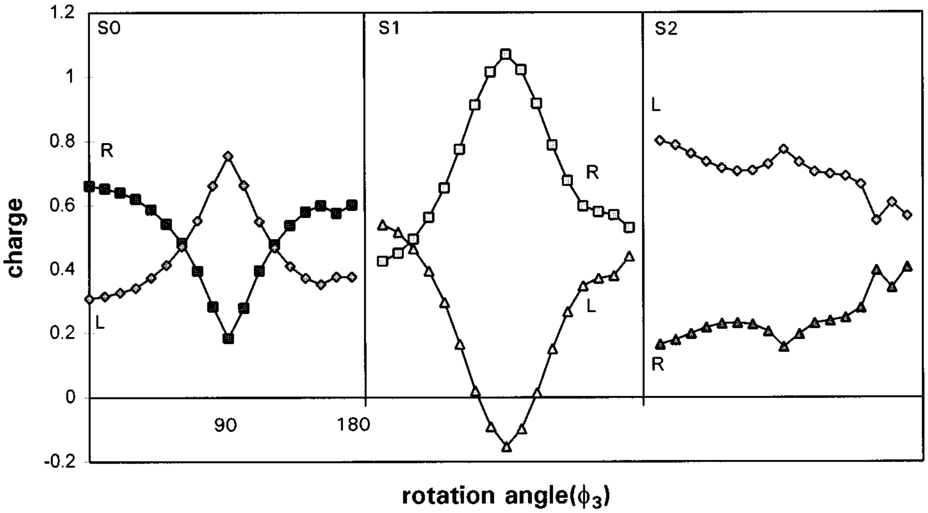

Figure 4. Charge distribution of the S_0, S_1, and S_2 states of HR as a function of rotation about the central double bond (ϕ_3). The molecule is divided into two parts (L, R) from the central double bond. L contains C9, the aniline ring, and dimethylamino group; R contains C8, the pyridyl ring, and methyl group.

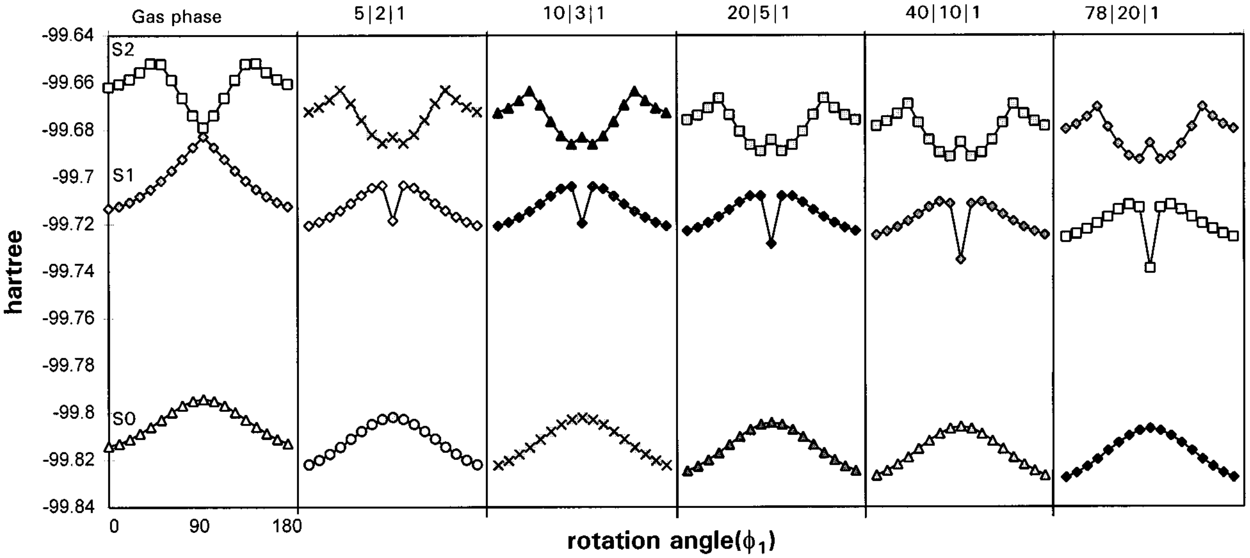

Figure 5. Change of energy levels of the S_0, S_1, and S_2 states of HR along with the dielectric constant of the solvent, rotation of the dimethylamino group (ϕ_1). For more explanation, see caption of Figure 3.

The shape of the energy curves for ϕ_1 rotation in the S_1 and S_2 states of HR is different from that of DMABN. For the gas-phase HR molecule, the avoided crossing of the S_1 and S_2 states occurs at 90°, while in DMABN it occurs at about 45°.[8] In the gas phase, there is a local energy minimum in the FC region in the S_1 state and the perpendicular conformation is at the energy maximum. If solvation is taken into account, a local energy minimum in the perpendicular conformation is created and there is avoidance between S_1 and S_2 in the 90° conformation. The energy of the S_1 state at the 90° conformation is further decreased in more polar solvents. When the dielectric constant of the solvent is greater than 20, the energy of the S_1 state at the perpendicular conformation is lower than that in the FC region. The shape of the S_1 potential energy curve in dielectric solutions presents some typical features of TICT state formation. Looking at the charge distribution of the S_1 state (Figure 6), we find that the 90° conformation is a charge transfer state.

The effect of solvation on the energy barrier in the S_1 state is also apparent from Figure 5 and Table 3. In more polar solvents, the barrier to rotation of the dimethylamino group in the S_1 state is lower and the energy of the TICT state is also further decreased. In aqueous solution ($\epsilon = 78$), the energy barrier is 0.0138 hartree compared to 0.0296 hartree when $\epsilon = 5$, and the energy of the TICT state is 0.0134 hartree lower than that of the planar conformation. But even in aqueous solution, the energy barrier for TICT state formation is still much higher than room-temperature energy.

Figure 6 shows the charge distributions of the S_0, S_1 and S_2, states. It is obvious that when the dimethylamino group is rotated, there is little charge transfer in the ground state. But in the first excited state, when the molecule is close to the perpendicular conformation, there is intramolecular charge transfer from the dimethylamino group to the rest of the conjugated system. In more polar solvents, the solvation favors this charge transfer state by lowering the energy of the S_1 state of the perpendicular conformation. So in polar solvents there might be a TICT state formed by twisting the dimethylamino group to the perpendicular conformation. But due to the relatively high energy barrier, the possibility of TICT state formation is small. The TICT state here has different characteristics from the TICT state formed in DMABN.[5,6,8] In DMABN, solvation effects bring the S_1 and S_2 states closer

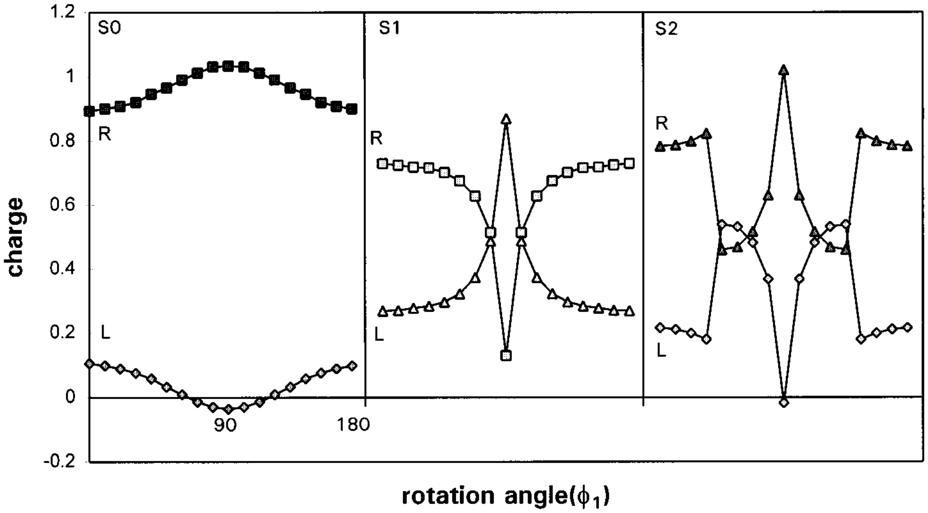

Figure 6. Charge distribution of the S_0, S_1, and S_2 states of HR, rotation of the dimethylamino group (ϕ_1). The molecule is divided into two parts (L, R) from the bond connecting the dimethylamino group and the aniline group. L is the dimethylamino group; R contains the aniline ring, ethylene, the pyridyl ring, and methyl group.

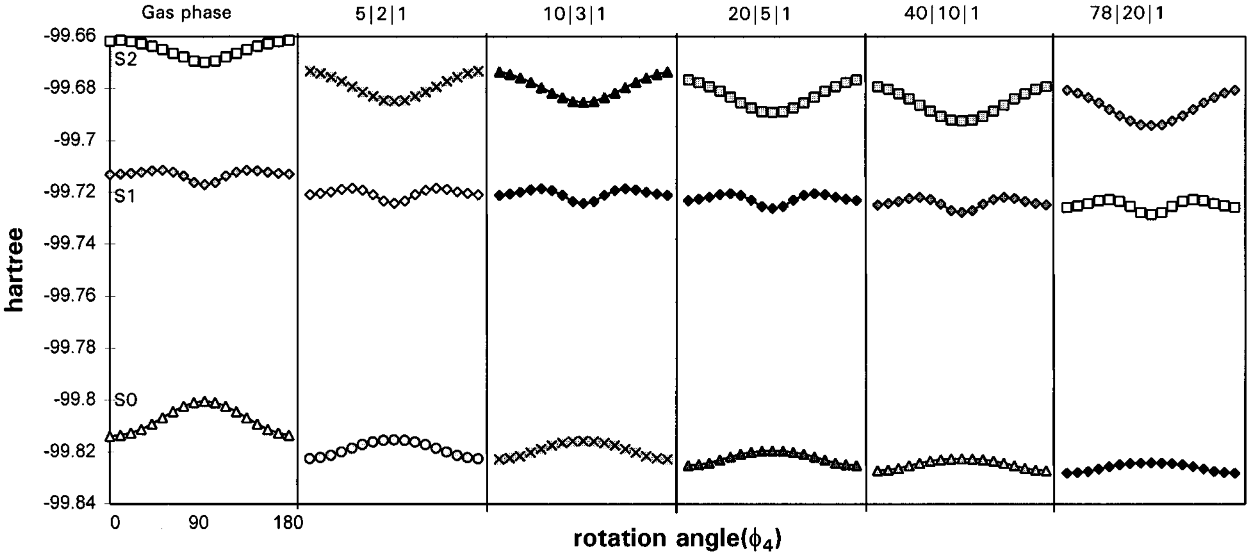

Figure 7. Change of energy levels of the S_0, S_1, and S_2 states of HR along with the dielectric constant of the solvent, rotation along the pyridyl–ethylene bond (ϕ_4). For more explanation, see caption of Figure 3.

together in more polar solvents, and by mixing the charge transfer S_2 state into S_1 state, a TICT state is formed. In the case of HR, the S_1 and S_2 states exhibit mixing in the gas phase when the dimethylamino group is at the perpendicular conformation. Solvation effects lower the energy of the S_1 state in the perpendicular geometry.

3.4. Rotation of the Pyridyl Ring. In HR there are also two single bonds that may be involved in a twisting mechanism. For stilbene-like molecules, it has sometimes been assumed that the TICT state is formed by twisting around these single bonds,[19,20,26] but there is no theoretical evidence for the TICT state being formed in this way. Energy curves of S_0, S_1, and S_2 of HR along the rotation of the pyridyl ring (ϕ_4 in Figure 1) are shown in Figure 7.

The barrier to rotation ϕ_4 is quite high for the ground-state molecule in the gas phase, about 0.013 hartree or 34 kJ/mol. However, increasing the polarity of the solvent decreases this barrier height (see also Table 3). In aqueous solution ($\epsilon = 78$), the barrier height is 0.004 hartree. Rotation in the ground state will enhance charge separation and cause the positive charge to be more concentrated on the pyridyl ring in more polar solvents. The decrease of this energy barrier in more polar solvents is consistent with the assumption that in more polar solvents the benzenoid form dominates in which the pyridyl–ethylene bond is more single bond like and rotation around that bond should be easier.

When the molecule is excited, there is a local energy minimum in the FC region. The barrier for the planar excited molecule to achieve the perpendicular conformation in the gas phase is 0.0015 hartree, which is on the same order as room-temperature energy. So in the gas phase, excited molecules should be able to undergo rotation around this bond and achieve the perpendicular conformation. Solvation will increase this energy barrier, but the effect is relatively small. In solvents with $\epsilon = 20$, the energy barrier is about 0.0028 hartree.

As shown in Figure 8, S_1 is a charge transfer state, and the positive charge center changes from the pyridyl ring in the ground state to the aniline ring in the excited state. Twisting the pyridyl group to the 90° position enhances this charge transfer. However TICT state formation is only expected when the twisted conformation is more stable than the FC geometry, and for HR the energy difference is small for this rotation.

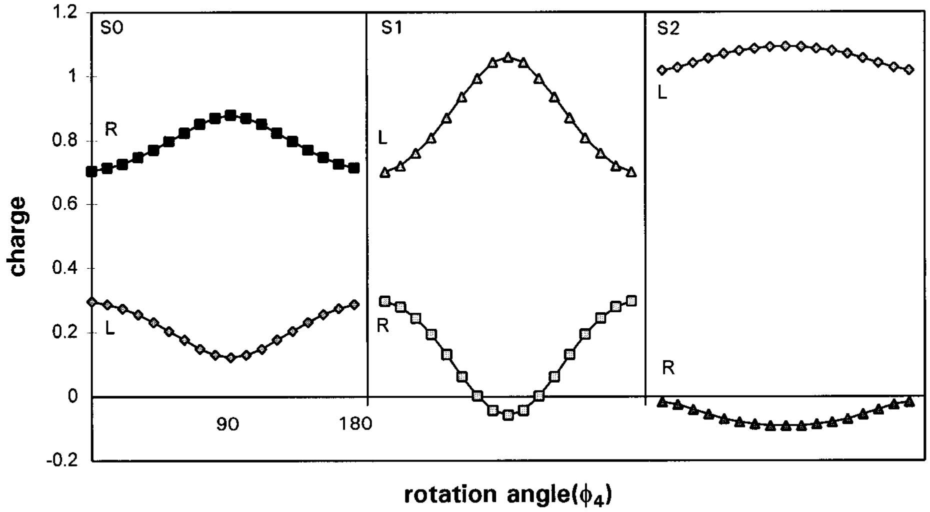

Figure 8. Charge distribution of the S_0, S_1, and S_2 states of HR, rotation along the pyridyl−ethylene bond (ϕ_4). The molecule is divided into two parts (L, R) from the pyridyl−ethylene bond. L contains the dimethylamino group, aniline ring, and ethylene; R contains the pyridyl ring and methyl group.

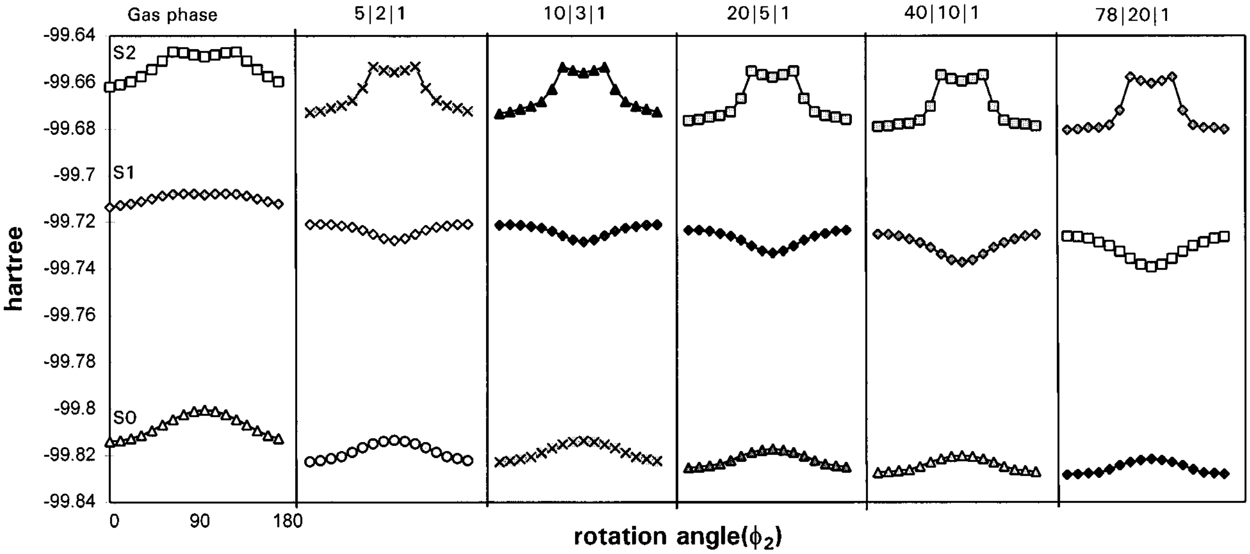

Figure 9. Change of energy levels of the S_0, S_1, and S_2 states of HR along with the dielectric constant of the solvent, rotation along the aniline−ethylene bond (ϕ_2). For more explanation, see caption of Figure 3.

3.5. Rotation of the Phenyl Group. Figures 9 and 10 show the energy curves and charge distributions when the aniline ring is rotated around the ethylene−aniline bond (ϕ_2 in Figure 1). Some of the energy barrier data are summarized in Table 3. They exhibit some similarities with those of rotation of the pyridyl ring and also some different features.

For the gas-phase molecule in the ground state, the phenyl group rotation is hindered, with an energy barrier of 0.013 hartree at 90°. Solvation will lower the barrier height but not as effectively as in the case of rotation of the pyridyl ring (Table 3). So even in aqueous solution, the barrier height is still 0.0068 hartree. The decrease of energy barrier in more polar solvents is also consistent with the assumption that in more polar solvents the benzenoid form dominates. Compared to the pyridyl−ethylene bond, the rotation about the aniline−ethylene bond is less dependent on solvent polarity.

In the gas phase, when the molecule is excited, there is a local energy minimum in the planar conformation. The barrier height for rotation of the aniline group is 0.0045 hartree, and the aniline group is not allowed to freely rotate in the S_1 state.

In solution there is no barrier to rotation around ϕ_2 in the S_1 state. Thus upon excitation to S_1 the aniline ring will rotate to the perpendicular conformation due to thermal fluctuations.

As shown in Figure 10, rotation of the aniline ring enhances the charge transfer in the S_1 state. At the perpendicular conformation, the molecule has the largest charge transfer. This is also characterized as a TICT state. But the effect of rotation of the aniline ring and pyridyl ring on the charge transfer is different from that of rotation of the dimethylamino group. In the former case, major charge transfer has happened in the planar conformation in the S_1 state and rotation of the aniline ring or the pyridyl ring just enhances the charge transfer. But in the case of rotation of the dimethylamino group, there is little charge transfer from the dimethylamino group in the planar conformation and rotating the dimethylamino group to the perpendicular conformation leads to nearly complete charge transfer from the dimethylamino group to the rest of the conjugated system.

3.6. Solvation Effect and TICT State Formation. Solvation lowers the energies of all conformations, as expected for ionic species, and increases the vertical energy difference between the ground (S_0) and excited states (S_1) in the Franck−Condon region ($E_{S_1} - E_{S_0}$ in Table 3). The calculations

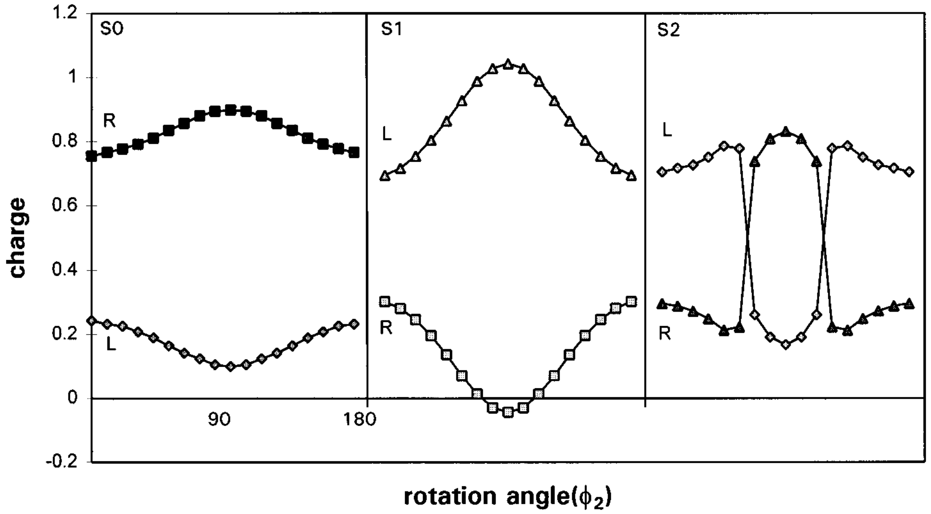

Figure 10. Charge distribution of the S_0, S_1, and S_2 states of HR, rotation along the aniline−ethylene bond (ϕ_2). The molecule is divided into two parts (L, R) from the aniline−ethylene bond. L contains the dimethylamino group and aniline ring; R contains the ethylene, pyridyl ring, and methyl group.

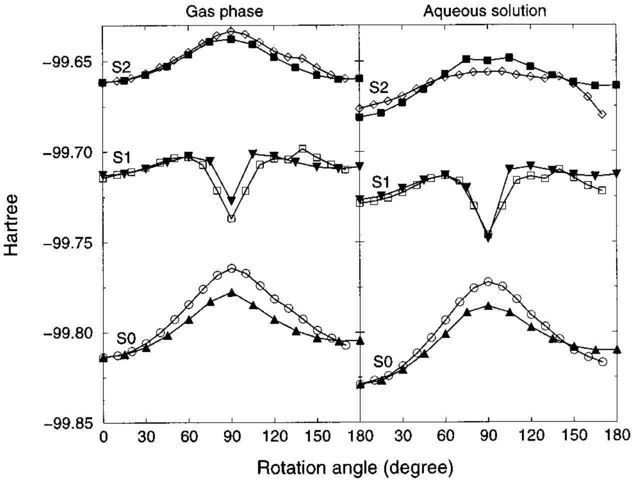

Figure 11. Energy of the S_0, S_1, and S_2 states of HR as a function of rotation about the central double bond in gas phase and aqueous solution. The open symbols are from calculations in which the geometry is kept fixed except for the rotation angle. The filled symbols represent results from calculations in which the geometry is optimized with respect to all other conditions.

presented here are in accord with the observed blue shift of the absorption maxima with increasing solvent polarity, as shown in Table 1. As shown in Table 2, the $S_0 \rightarrow S_1$ transition is accompanied by the transfer of negative charge from the aniline ring to the pyridyl ring. The charge distribution in the excited state is more delocalized than in the ground state. Thus the ground state is stabilized more than the excited state, and λ_{abs} shifts to the blue, as solvent polarity increases.

TICT state formation can also be used to explain experimental fluorescence results. The decrease of fluorescence yield of HR in more polar solvents could be related to the formation of the nonradiative TICT states. Görner et al.[14] observed that the fluorescence maximum shifts to lower wavelength and the fluorescence yield also decreases when the temperature is lowered. At low temperature, the molecule tends to be in lower vibrational levels and internal rotation becomes more hindered due to increase in solvent viscosity. Therefore, the TICT state is harder to form at lower temperature.

3.7. Effect of Allowing the Rest of the Molecule To Relax. The calculations presented so far were performed as a function of rotation about one chemical bond, keeping the rest of the molecule fixed. While this assumption might not be true in reality, it allows us to separate the effect of the rotation around one chemical bond from the effects of other rotations. At present, it is impossible to include solvent effects in the molecular geometric optimization. To search a global energy minimum including solvent effects would increase the computational time by several orders of magnitude, since there are four internal rotational degrees of freedom.

To explore the possibility of TICT state formation, calculations that vary only the internal rotation angle are conceptually useful. However, to see if the working assumption could influence our conclusions, we performed another set of calculations of the excited-state energy as a function of internal rotation, allowing the rest of the molecule to relax in the gas phase. This was done by optimizing the molecular geometry at fixed values of the angle of internal rotation. There is little effect on the overall charge distribution on the molecule. The optimized geometries obtained in this way are very similar to those used in the calculations discussed above. Allowing the rest of the molecule to relax introduces the effects due to other rotations, as reflected by small rotational angles around other chemical bonds (<3°) and small ring deformation in the optimized geometries in some cases. These effects should be kept in mind when looking at the following results.

Figures 11−14 show the comparison of two calculation methods. The filled symbols are the results obtained when the rest of the molecule is allowed to relax. In all the cases, we obtain results that are qualitatively consistent with our previous assumption in which the rest of the molecule is kept rigid.

In the gas phase, allowing the rest of the molecule to relax decreases the barrier to internal rotations in the ground state. In the S_1 state, the barriers for rotation around the aniline−ethylene and pyridyl−ethylene bonds are increased.

There are some interesting phenomena when the molecule is allowed to relax in aqueous solution. In the ground state, except the rotation around the central double bond, the barriers for rotations around the other three bonds are further decreased compared to the gas phase. While this is as expected, one interesting phenomenon for rotations around the aniline−ethylene and pyridyl−ethylene bonds is the occurrence of another energy minimum corresponding to about 50° rotational angle. In the case of rotation of the aniline ring, the barrier to

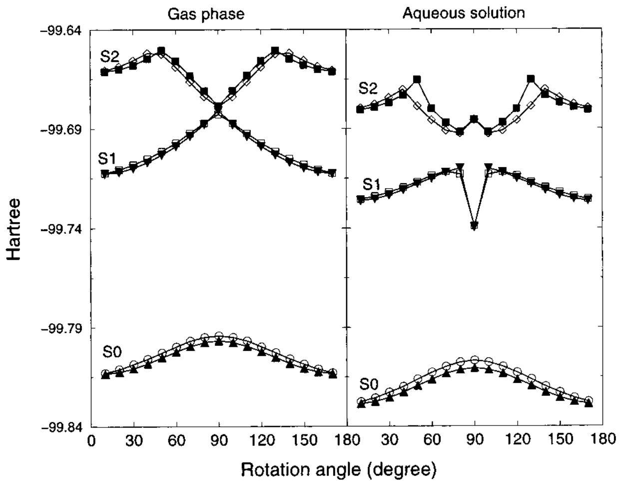

Figure 12. Energy of the S_0, S_1, and S_2 states of HR as a function of rotation about the pyridyl−ethylene bond in gas phase and aqueous solution. For more explanation, see caption of Figure 11.

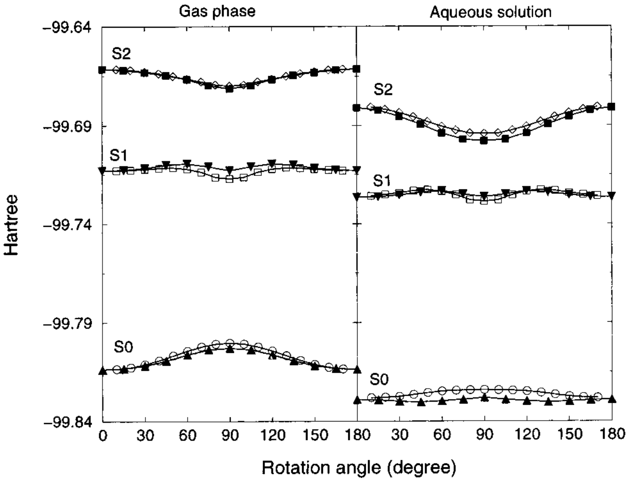

Figure 13. Energy of the S_0, S_1, and S_2 states of HR as a function of rotation of the dimethylamino group in gas phase and aqueous solution. For more explanation, see caption of Figure 11.

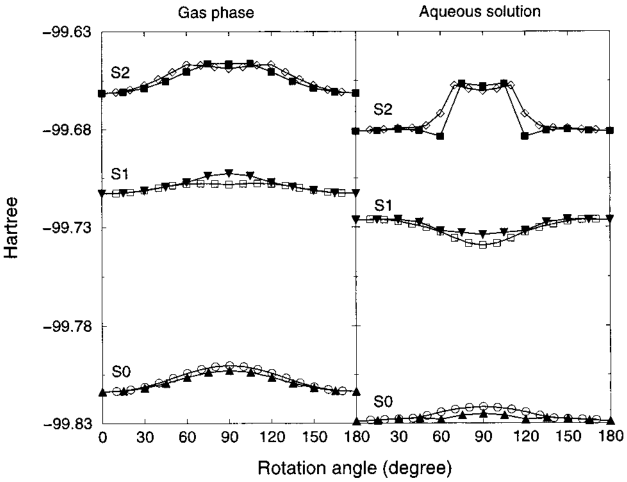

Figure 14. Energy of the S_0, S_1, and S_2 states of HR as a function of rotation about the aniline−ethylene bond in gas phase and aqueous solution. For more explanation, see caption of Figure 11.

achieve this energy minimum is 0.002 hartree, while for rotation of the pyridyl ring, there is no energy barrier. This suggests that large amplitude torsional motion of the aniline and pyridyl rings takes place in strongly polar solvents such as H_2O.

4. Conclusion

Quantum chemical calculations combined with a cylindrical solvation model have been used to investigate the possibility of TICT state formation by rotating part of the molecule about several chemical bonds.

There might be three different channels of TICT state formation in HR. According to the energy barrier height and the energy of the TICT state relative to that in the FC region, the rotation around the aniline−ethylene bond should be the easiest since there is no barrier to rotation in the S_1 state in solution. The rotation around the pyridyl−ethylene bond is also possible but not so favored by solvation effects, and rotation of the dimethylamino group should be the most difficult.

The high-energy barrier to rotation around the central double bond in the S_1 state is consistent with the low photoisomerization yield of HR in most of the solvents. The small observed quantum yields for photoisomerization might be due to the coupling of the torsional vibration to other Franck−Condon active modes.

The calculations account for most of the experimental results. The absorption maximum is predicted to shift to the blue in more polar solvents. The results of this work can be compared to the previous suggestion that increasing solvent polarity favors the contribution of the benzenoid resonance form.[15,17,18] This conclusion was based on the observed solvent shift of the stretching frequency of the central C=C bond. In support of this conclusion, the ground-state barrier to rotation about the −C=C− bond was found in this work to increase with solvent polarity. The barriers to rotation of the phenyl and pyridyl groups were found to decrease with solvent polarity, also in agreement with the model. However, the barrier to rotation of the dimethylamino group was observed to increase with solvent polarity, in contradiction to expectations of the resonance form model. This may be due to the fact that solvent interactions and steric effects also influence the energy barrier for rotation about a bond.

The excited-state barriers calculated in this work are slightly overestimated, due to the fact that the molecule was kept rigid except for rotation about a particular bond. But this strategy allows us to separate the effect of a single rotation from other rotations. The energy barrier for rotations in the ground state are decreased by allowing the molecule to relax in the gas phase. This might be a little more realistic, but it introduces the effects of other rotations that might not be appropriate to be ascribed to the rotating bond. It was found that allowing the molecule to relax along the remaining internal coordinates made little difference to the qualitative conclusions.

The nature of the emitting state (TICT vs locally excited) remains in question. With the exception of the ϕ_2 rotation, excited-state barriers to internal rotation are high compared to thermal energy. None of the torsional modes are calculated to be displaced in the S_1 state, so Franck−Condon (FC) activity is precluded. Thermalization of higher frequency FC-active modes *could* lead to TICT state formation along ϕ_1, ϕ_3, and ϕ_4. However, as reported elsewhere,[16] the total internal reorganization energy is less than the excited-state torsional barriers, except for ϕ_2, for which there is no barrier to internal rotation. We suggest that emission takes place from a configuration that is relaxed with respect to rotation ϕ_2 of the aniline ring. Further investigations pointing to this conclusion, along with consideration of solvent dynamical effects on the spectra of HR in water, are reported elsewhere.[16]

The results of this work point out the importance of solvent effects on the excited-state dynamics of HR. Of particular interest is the different line width of HR in different solvents, which reflects the importance of solvent dynamics in the line-broadening mechanism. Resonance Raman studies of the solvent dynamics on the intramolecular charge transfer of HR in aqueous solution will be reported elsewhere.[16]

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