secondary NH_3 may form a six-membered cylical structure by bonding to the phenoxy oxygen atom, thus reducing the number of free hydrogen sites to four. It is unclear, however, whether a cyclical structure is stable since it requires bending hydrogen bonds, nor is there evidence of a blue shift upon addition of the second NH_3 as expected for a proton donor bond to phenoxy.³⁶

7. Summary and Conclusions

The goal of this work is to gain information on the solvation of chemical reactions, on a molecular level, through time-resolved studies of molecular clusters. The work presented here underscores the importance of solvent structure. We summarize our results in the following:

1. Ground electronic ion-pair states of phenol, stabilized in $(NH_3)_n$ solvent clusters, were detected that have long-lived absorption at 355 nm and ionize to PhOH⁺ $(NH_3)_n$ and H⁺ $(NH_3)_n$. The absorption corresponds to a known ion-pair transition of solvated PhO⁻H⁺. The detected ions show a strong enhancement at n = 4 and 5, corresponding to a stable closing of the first solvent coordination shell. The ground electronic state value of K_a is very small at n = 5 but increases with n; hence, much of the signal may originate from ion-pair excitation of large values of n, which then evaporate to stable cluster sizes upon ionization.

2. No evidence of solvent-separated ion pairs was observed. The yield of negative ions (e.g., PhO^{-}) expected from photodissociation of SSIPs was at least 3 orders of magnitude less than the positive ions formed by the competitive process of dissociative ionization of CIPs. These results are consistent with calculated Coulomb potentials and the low dielectric (bulk) polarization of these small clusters.

3. The formation of phenol dimer inhibits the rate of ESPT to the solvent cluster relative to the monomer. The self-association in the dimer prevents at least one of the hydroxy protons from bonding directly to the solvent.

4. Solvent bonding structures were deduced from resonanceionization mass spectra of PhOH in mixed solvent clusters $(NH_3)_mB_n$. For B = CH₃OH, the solvent NH₃ forms the stronger bond to phenol; however, CH₃OH then preferentially fills the first coodination shell about the protonated NH₃. For B = TMA, the solute PhOH forms a stronger bond to TMA than to NH₃. However, TMA lacks hydrogen-bonding sites for solvent growth. Consequently, in larger mixed solvent clusters, NH₃ rather than TMA bonds to PhOH, thus providing hydrogen-bonding sites for overall solvent stability.

Molecular cluster studies provide a bridge to understanding the relation between gas-phase and solution-phase chemistry. It is not obvious that there is a connection until one focuses on the gas-phase counterpart and examines how the potential curves change by sequential addition of solvent molecules. The solvation properties in solution then follow clearly from the cluster analogy.

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Proton Transfer in the Inter- vs Intramolecular Quenching of Naphthol Fluorescence by Amines[†]

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"Charge-transfer" quenching of naphthols by amines can occur via either proton transfer or electron transfer. To gain insight into the quenching mechanism, the room temperature photophysics of 2-naphthol (N2) in the presence of a trialkylamine was compared with that of 2-methoxynaphthalene (N2M) and of an intramolecular equivalent, 1-[(dimethylamino)methyl]-2-naphthol (1DMN2). To maintain structural analogy, dimethylbenzylamine (DMBA) was used as the quencher. Comparison of steady-state and time-resolved fluorescence for both intermolecular and intramolecular cases leads to the conclusion that the major quenching pathway involves proton transfer.

The adiabatic proton transfer of photoexcited naphthols to amines has been the subject of intense scrutiny.1 At room temperature, the fluorescence of naphthalene derivatives, including naphthols, is efficiently quenched by alkyl amines.² The mechanism of such quenching has been the subject of much discussion, and the issue is by no means resolved. It has been common practice, therefore, to refer to such quenching as "charge-transfer" quenching without specifying the identities of the charged species involved in such quenching. The difficulty arises because two opposing mechanisms can operate for naphthols. This mechanistic dichotomy is represented in Figure 1. On the one hand, naphthols undergo an enhancement of acidity upon photoexcitation.³ The resulting pK_a^* 's, which range from 0 to 2, provide sufficient driving force for adiabatic proton transfer to amine (k_{pt}) within the lifetime of the excited state. On the other hand, naphthalenes in general undergo electron-transfer quenching (k_{et}) , presumably to form nonemissive ion pairs. For both of these processes, the intervention

[†]Dedicated to Prof. Michael Kasha in honor of his 70th birthday.

of hydrogen bonding prior to proton or electron transfer may affect the excited-state dynamics.

One possible distinguishing feature of the two mechanisms is the requirement that the naphtholate anion be an obligatory intermediate following proton transfer. Thus, the presence of naphtholate emission might provide a method for discerning the intervention of proton transfer. However, other processes within the resulting ion pair, particularly nonadiabatic back proton

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Figure 1. Electron- vs proton-transfer quenching of 2-naphthol.

transfer (k_{bot}) , can lead to rapid excited-state deactivation without significant anion emission. Although numerous studies have been carried out on each of these issues, an examination of a system in which all of these elements were present simultaneously was in order.

Background

The importance of H bonding cannot be overlooked when the dynamics of proton transfer are determined. There are numerous reports of the role of solvent in the H-bonding equilibrium between aromatic alcohols and amines.^{4,5} Most frequently, these studies involve the evaluation of electronic absorption spectra as a method of studying the electronic properties of the ground state as well as the thermodynamics of the H-bond formation. Typically, H bonding is evinced by changes in both the wavelength and the intensity of an electronic transition, although this is not a requirement. Baba and co-workers have studied the effect of dioxane on the absorption spectra of 1- and 2-naphthol in isooctane at 20 °C.6 They note a broadening in vibrational structure upon H-bond formation, although there remains the similarity of sharp vibrational components in the presence of the proton acceptor. Nagakura and co-workers have investigated the effect of H bonding on the near-UV absorption spectra of 1- and 2-naphthol where triethylamine was used as the proton acceptor⁷ and have suggested that the nature of the H bond shared between naphthol and amine is a combination of electrostatic and charge-transfer forces. Kubota has drawn the same conclusions from similar experiments. However, he goes so far as to infer that the charge-transfer characteristics are related to the enhanced photoacidity of naphthol.⁸ The electron migration of the 2p π electrons on the oxygen atom of the naphthol to the aromatic ring is larger in the ${}^{1}L_{h}$ state than the ground state; therefore, the net positive charge on the oxygen atom increases in the ${}^{1}L_{b}$ state. This is thought to lead to a more stable H-bonding complex in the excited state and hence a greater photoacidity.

The origin of the broadening in the absorption spectra when an amine is added has been attributed to the nature of excited states of the H-bonding system. For example, Mataga has studied the H-bonding of triethylamine with 2-naphthol (N2) in benzene and *n*-heptane.9 He reports a significant red shift in the fluorescence spectra, especially in benzene, as compared to the absorption spectra. He concludes that the ${}^{1}L_{b}$ equilibrium state of the naphthol has considerable charge-transfer character of the type described by Kubota. The mixing of a charge-transfer state would perhaps modify the potential energy surface in the excited state, thereby broadening the spectra of the H-bonded species.

The effect of H bonding can be seen in fluorescence spectra as well as absorption spectra. Since fluorescence is emitted from an equilibrium excited state to the Frank-Condon ground state, one might expect a shift to longer or shorter wavelengths, depending on the strength of the H-bonding interaction in the excited state and the ground state. It is well established that the Hbonding interaction ability of aromatic alcohols and amines is stronger in the lowest excited singlet state than in the ground state. Mataga has addressed the issue of H-bond formation in the excited state where the proton is capable of conjugating within a π -electron system.¹⁰ For proton donors such as N2, aniline, and pyrrole, the fluorescence yields decrease in the presence of nitrogen heterocycles reportedly due to the nonradiative degradation of the excited state by means of delocalization of π electrons through the H bond. For example, pyridine effectively quenches the fluorescence of N2 in alcoholic and aqueous solutions, as well as that of 2-methoxynaphthalene (N2M). Mataga concludes that the H-bonding nature of the medium aids in the role of the H bonding in the fluorescence quenching and that this quenching may be attributed solely to the presence of the hydrogen bond.

Koizumi has questioned Mataga's conclusions after finding that naphthol and methoxynaphthalene are both quenched in the presence of quinoline and pyridine in *n*-hexane.¹¹ The conclusion drawn was that H bonding is not always necessary for quenching, but the results were consistent with the notion of charge transfer from fluorescer to quencher.

For any process that involves photoexcitation in a system containing a fluorophore and an acceptor of comparable redox potential, the possibility of electron-transfer quenching cannot be overlooked. In general, two types of electron-transfer quenching can be observed. In the first type, which is typical for quenching processes involving amines, an exciplex is formed and can be recognized by the presence of a broad, structureless emission red-shifted from the emission characteristic of the parent fluorophore. In the second type, a very efficient quenching occurs without appearance of a new emission.¹² Increasingly, the difference between the two types has been ascribed to contact vs solvent-separated ion pairs.¹³ An excellent model system is provided by Chandross and Davidson in their studies of the emissive properties of 1- and 2-[(dimethylamino)methyl]naphthalene.¹⁴ Interestingly, the fluorescence of each is almost totally quenched at 25 °C, unlike their longer methylene chain counterparts where intramolecular exciplex emission is seen. Chandross reasons^{14a} that, in the compounds with a single methylene spacer, quenching need not involve exciplex formation but rather the exciplex state, whose energy must lie appreciably lower than that of the quenching configuration.

Haslinger and Wolschann have prepared Mannich bases of naphthols to study intramolecular H bonding and its role in photoinitiated proton-transfer reactions.¹⁵ In their studies, as in ours, the proton acceptor is isolated from the photoacid by a methylene unit, avoiding the ambiguity of phototautomerization in conjugated systems. Their studies involved synthesis of piperidino, morpholino, and pyrrolidino derivatives of 1- and 2naphthol. Interestingly, the piperidino adduct of 1-naphthol demonstrated anionic emission in cyclohexane, acetonitrile, and ethanol. The 2-naphthol derivative did not follow suit, giving neutral emission in cyclohexane while anionic emission dominated in acetonitrile and ethanol. Although 1-naphthol $(pK_a^* = 0.5)$ has a greater photoacidity than 2-naphthol ($pK_a^* = 2.5$), it is interesting that the 1-naphthol adduct demonstrates protontransferring ability in a solvent that typically does not favor proton transfer.

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CHART I



Figure 2. Effect of increasing DMBA concentration on absorption spectrum of N2 in cyclohexane.

Photoinitiated proton transfers can proceed by two different mechanisms: within a hydrogen-bonded ground-state complex or by means of a dynamic reaction involving mutual diffusion of the reagents. Kuz'min and co-workers have investigated the proton-transfer dynamics of the naphthol-amine system in a butyronitrile glass which, at 77 K, eliminates diffusion.¹⁶ They report that, under appropriate thermodynamic conditions in a polar and readily polarizable aprotic solvent, butyronitrile, there exists no appreciable potential barrier to excited-state proton transfer in the solid state. These studies have also been applied to the solution dynamics of this system by monitoring the time-resolved kinetics of excited-state proton transfer.¹⁷ Kuz'min concludes that radiationless energy degradation takes place after proton transfer within the hydrogen-bonded complex. On the basis of this results, Kuz'min proposed two mechanisms to explain the electronic degradation in hydrogen-bonded ion pairs.^{17b} The first mechanism implies that the back reaction of the proton transfer in an ion pair leads to formation of a hydrogen-bonded excited complex in which degradation of the electronic excitation energy occurs with a high probability. The second mechanism suggests that the degradation of electronic excitation energy in the ion pairs is a result of donor-acceptor interactions between the gegenions. In such a case the quenching may be due to an energy barrier that is overcome by the gegenions, allowing a configuration which ensures a maximum probability of rapid electron transfer. Kuz'min was not able to draw a conclusive argument for either mechanism.

To examine these competing mechanisms, we wanted an intramolecular proton acceptor of the Mannich type explored by Haslinger and Wolschann,¹⁵ but one which also maintained analogy with other trialkylamine quenchers and which was structurally analogous to the [(dimethylamino)methyl]naphthalene system investigated by Chandross.¹⁴ We chose 1-[(dimethylamino)methyl]-2-naphthol (1DMN2), which provides comparison with the kinetically well behaved 2-naphthol (N2) and the methyl ether of N2, 2-methoxynaphthalene (N2M), which has nearly identical electronic properties but is not a photoacid. Finally, to minimize differences due to different basicity and structure, we

TABLE I: Stern-Volmer Constants (K_{SV}, M^{-1}) for Quenching of N2 and N2M by DMBA

	-	•		
	solvent	N2	N2M	
_	cyclohexane	167 ± 14	0 ^a	
	benzene	7.35 ± 0.07	0.588 ± 0.021	
	acetonitrile	14.2 ± 0.1	2.84 ± 0.02	
	ethanol	1.62 ± 0.08	0.975 ± 0.076	
	Me ₂ SO	1.67 ± 0.02	3.12 ± 0.09	
	-			

^aA small increase in emission was observed with DMBA.



Figure 3. Solvent dependence of 1DMN2 emission.

chose as our proton acceptor the amine most congruent with 1DMN2, namely, *N*,*N*-dimethylbenzylamine (DMBA) (Chart I).

Results

Determination of Equilibrium and Stern-Volmer Quenching Constants of 2-Naphthol and N2M with DMBA. Of the solvents examined, only benzene and cyclohexane gave noticeable spectroscopic changes upon addition of DMBA to solutions of N2. Figure 2 shows the absorption changes of N2 upon addition of DMBA in cyclohexane. The vibrational structure in cyclohexane is pronounced, with isosbestic points indicating a 1:1 complex between naphthol and amine. DMBA does not have as dramatic of an effect on the absorption changes in benzene nor do isosbestic points appear. Using the changes in absorptions observed in the range 320-350 nm, equilibrium constants for the N2/DMBA hydrogen-bonded complex were determined in cyclohexane (82 L M^{-1}) and benzene (26 L M^{-1}).

In contrast to the absorption results, which showed effects only in benzene and cyclohexane, the effects of DMBA on the fluorescence emission of N2 in benzene, acetonitrile, and Me₂SO were dramatic. In acetonitrile and Me₂SO a new peak appeared around 450 nm which corresponds to the naphtholate anion.¹⁸ An increase in emission intensity at 450 nm was also observed in benzene, while in cyclohexane only quenching of the neutral was observed. In no case did the intensity increase for the longwavelength emission match the intensity lost from the neutral emission. Similar studies using N2M yielded quenching only. In all solvents but cyclohexane, linear Stern–Volmer kinetics with DMBA were observed. The SV coefficients are reported in Table I. Quenching of N2 in cyclohexane was second order. The results indicate that fluorescence quenching occurred to a minor extent in acetonitrile and Me₂SO.

Absorption and Fluorescence Studies of 1-[(Dimethylamino)methyl]-2-naphthol (1DMN2). The absorption spectrum of 1DMN2 mirrors the excitation spectrum, neither of which differs significantly from that of the parent N2. Unlike the excitation spectrum, the behavior of the fluorescence emission is solvent dependent (see Figure 3). For example, in cyclohexane the emission of 1DMN2 is attributed exclusively to the neutral, with maxima at 365 and 378 nm. The shape of this emission is similar to that of N2, although significant broadening is noted in the

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 TABLE II: Comparison of 1DMN2 Emission and 2-Naphtholate

 Emission

	λ_{max} , nm	
solvent	2-naphtholate, sodium salt ^a	1DMN2
benzene	427 ^b	418
acetonitrile	451	436
ethanol	420	426
Me ₂ SO	456	443

^{*a*} From ref 18. ^{*b*} Contains crown ether.

 TABLE III: Effect of DMBA on N2 Neutral Emission and Average Lifetime



Figure 4. Effect of varying benzene composition on emission of 1DMN2 in cyclohexane.

former, a result of strong hydrogen bonding. In benzene, acetonitrile, EtOH, and Me₂SO, emission maxima were produced at 418, 436, 426, and 443 nm, respectively (see Table II). These emissions show the general solvent effects associated with ion pairs involving naphtholate anion.¹⁸ A small amount of neutral emission was noted at 361 and 366 nm in EtOH and Me₂SO, respectively. To investigate the nature of photoexcited 1DMN2 further, a mixed-solvent study was conducted. Samples were prepared in 0-60% benzene-cyclohexane mixtures. The results from the steady-state experiment are found in Figure 4. A broad and featureless emission appeared with a maximum at 389 nm at low benzene concentration. At concentrations of benzene in cyclohexane above 10%, the new emission appeared only as a shoulder on a longer wavelength emission. This emission grew in intensity with increasing benzene concentration without any further spectral change. All emission maxima produced during the mixed-solvent study gave rise to identical excitation spectra, indicating a common ground-state fluorophore.

Time-Resolved Measurements of 1DMN2 and of N2 with DMBA. Further information about the excited state of N2 in the presence of DMBA and of 1DMN2 is provided by the fluorescence lifetime measurements. Second-exponential decays were observed for N2 with and without DMBA (see Table III)¹⁹ and for 1DMN2 in ethanol. In all of the solvents examined, the decay rate of 1DMN2 was found to be faster than that of N2, which has a reported lifetime of 8.0 ns in benzene.^{17c} In cyclohexane, the neutral emission decayed with a lifetime of 3.9 ns. This lifetime did not vary at longer wavelength emission monochromator was set at 426 nm, corresponding to anion emission, a single exponential decay with a lifetime of 2.5 ns was observed.





1 (EtOH) = 7.0 n

Figure 5. Z vs E forms of 1DMN2 in ethanol.

Discussion

The evidence presented here leads to the inescapable conclusion that the quenching of naphthol fluorescence involves proton transfer as the primary event followed by back proton transfer along the lines proposed by Kuz'min^{17b} but for which no definitive conclusion could be drawn. The contrasting behavior between N2M, for which only electron transfer is viable, and 1DMN2, for which proton transfer dominates, allows a compelling case to be made that the quenching of N2 itself involves a back proton transfer within an ion pair of a specific geometry. These conclusions are based upon the following observations.

1. Electron transfer between substituted naphthalenes and amines leads to ion pair formation and thus should be facilitated in polar solvents such as ethanol and Me₂SO. The quenching behavior of N2M by DMBA supports this expectation. However, proton transfer also produces ion pairs, yet naphthol and DMBA exhibit contrasting Stern-Volmer quenching behavior as a function of solvent polarity, with the most nonpolar solvent, cyclohexane, providing the highest quenching constant, K_{SV} , for naphthol and negligible quenching for methoxynaphthalene. A mild exception to this general trend is benzene, although quenching of naphthol fluorescence in this solvent still exceeds that of methoxynaphthalene. Moreover, benzene exhibits maximum quenching of naphtholate fluorescence as well. In solvents with high hydrogen-bonding character, for which hydrogen bonding between the amine and naphthol is disrupted, the quenching rate constants approach the same limiting value.

2. The fluorescence of 1-[(dimethylamino)methyl]naphthalene (1DMN) is strongly quenched due to the intervention of an exciplex,¹⁴ which may be associated with contact ion pair formation.¹³ However, the hydroxy derivative of 1DMN, i.e., 1DMN2, shows no such quenching, presumably because intramolecular hydrogen bonding raises the oxidation potential of the amino group and inhibits electron transfer. Rather, proton transfer occurs to yield anion emission. The new emission in 10% benzene-cyclohexane is reminiscent of the exciplex emission exhibited by similar substrates.^{13b,20} However, the anion emission shows the same bathochromic shift with increasing solvent polarity as does sodium naphtholate,¹⁸ although the fluorescence of the latter is red-shifted relative to 1DMN2, consistent with the formation of an ion pair of different structure for the latter. The diminished singlet lifetime for 1DMN2, relative to that of naphthol itself, is also consistent with proton transfer to yield an intramolecular ion pair, since naphtholate anion, as its sodium or potassium salt, exhibits a reduced lifetime in ion-pairing solvents.¹⁸

3. 1DMN2 also exhibits a dual exponential neutral decay in the only pure solvent, ethanol, for which both neutral and anion emission are observed. However, anion emission in this solvent has a rise time simultaneous with that of the neutral and shows a single exponential decay which coincides with neutral decay. This suggests the presence of two noninterconverting forms in the excited state, only one of which can lead to anion emission.

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Figure 6. Proposed quenching geometry for N2/DMBA ion pair.

Plausible candidates for the forms are the intramolecularly hydrogen bonded Z form and the intermolecularly hydrogen bonded E form (see Figure 5). Emission from the Z and E forms of 1-naphthol has been observed in the gas phase.²¹ Proton transfer within the Z form can occur more rapidly than our time resolution (<100 ps) or may be barrierless, as has been observed for naphthol-triethylamine complexes in the solid state.¹⁶

4. In contrast to the strong quenching of N2 fluorescence by DMBA, the N2 lifetime is only partially affected (see Table III). This is consistent with other observations that naphthol quenching by amines occurs mainly through pre-existing hydrogen-bonded complexes. Thus, the quenching of naphthol fluorescence is static rather than dynamic.

How then do we rationalize the divergent quenching of N2 and N2M as a function of solvent polarity? This divergence becomes clear if we assume that quenching of N2 fluorescence involves back proton transfer within the incipient dimethylbenzylammonium naphtholate ion pair of a particular geometry. Inasmuch as the 2-naphtholate excited state is known to possess intramolecular charge-transfer character,²² the resulting ion pair will be stabilized by closest approach of dimethylbenzylammonium and the distal naphtholate ring (see Figure 6). Quenching of the ion pair emission can involve either formal proton transfer to the keto form or partial proton transfer followed by rapid deactivation of the incipient keto form. Either mechanism of ion pair collapse would be facilitated in nonpolar solvents. In the case of 1DMN2, the methylene bridge prevents the intramolecular ion pair from attaining the required quenching geometry.

Back proton transfer has been shown to be operative in the quenching of 1-naphthol emission via the intermediate 1naphtholate anion and is accompanied by hydrogen/deuterium exchange in the distal ring.²³ Hydrogen/deuterium exchange has also been observed in the proton quenching of 1-methoxynaphthalene.²⁴ Such exchange is a sufficient but not necessary condition for proton quenching, however, inasmuch as H/D exchange requires proton removal from the opposite face of the molecule. Proton quenching of N2 via its conjugate base has also been observed under acid conditions.²⁵ In related studies, Shizuka has also demonstrated that low-temperature emission of 1naphtholate triethylammonium ion pairs produced by photoinduced proton transfer is characterized by two distinct ion pairs.²⁶ Thus, the inference that photoinduced proton transfer to alkylamines leads to distinct ion pairs, only one of which quenches the anion fluorescence, has a sound mechanistic basis. The use of 1DMN2 allows the conclusion to be drawn that the quenching geometry must allow considerable interaction between the distal naphthalene ring and the gegenion.

Experimental Section

Materials. Reagent grade 2-naphthol was sublimed and recrystallized repeatedly from petroleum ether or cyclohexane before use. Triethylamine, N,N-dimethylbenzylamine (DMBA), and all spectrophotometric solvents were purchased at 99+% purity

(Aldrich, Gold Label) and stored over 4-Å molecular sieves. Other solvents were singly distilled, stored over molecular sieves, and filtered before use. Synthetic samples were purified by highpressure liquid chromatography using a Rainin Dynamax column (60 A silica, 25 cm \times 1 cm diameter).

Instrumentation. Absorption spectra were recorded on a Gilford UV-vis spectrophotometer at a bandwidth of 0.5 nm. Fluorescence spectra were recorded using a SPEX Model F112X spectrofluorometer equipped with a xenon arc lamp and single grating excitation monochromator. Sample fluorescence was collected at right angles from the excitation beam with entrance and exit slit widths set at 1.0 mm. All spectra were corrected for the wavelength dependence of the photomultiplier response using a rhodamine B quantum counter. Samples were measured using 1.0-nm steps with an integration time of 0.5 nm/step. Concentrations were maintained between 10^{-4} and 10^{-5} M. The longest wavelength maximum in the excitation spectrum was used as the excitation wavelength. The purity of all samples was checked by monitoring the emission spectrum as a function of excitation wavelength. Fluorescence quantum yields were measured by ratioing the changing fluorescence emission maximum (of either neutral or anion) upon addition of quencher to that in the absence of quencher. First-order regression analysis of the Stern-Volmer plots yielded the quenching constants k_{SV} . In a few instances, second-order regression analysis was required. Temperature control was achieved with the aid of a Frigomix 1497 circulating bath.

¹H NMR (300 MHz) were recorded using a Varian Gemini spectrometer. Chemical shifts are reported in units of parts per million from internal tetramethylsilane.

Fluorescence Lifetimes. Excited-state lifetimes were measured with a time-correlated single photon counting fluorometer consisting of Photochemical Research Associates flashlamp and optics (PRA Model 510B high-voltage power supply, PRA Model 510B nanosecond lamp, and PRA Model 1200 sample box), double monochromators (Instruments SA, Inc., Model H10, on excitation, and Bausch and Lomb, No. 33-86-79, on emission). For stray light minimization, Hoya filters were used for the monitoring of sample fluorescence with a UV-36 used for neutral emission and an L-37 for anion. The emission photomultiplier tube (Hamamatsu, Model R928/115/387) was cooled with a thermoelectric housing and cooler (Products for Research, Danvers, MA). A modified Ortec 935 Quad CFD was used for conversion of photomultiplier pulses to fast NIM logic signals, which drove an Ortec Model 566 time-to-amplitude converter (TAC). The voltage pulses from the TAC were digitized by an Ortec multichannel analyzer. A Tennelec 850 precision time calibrator was used to calibrate electronics. Fluorescence lifetimes were determined by an iterative deconvolution technique using both a lamp scattering profile and the experimental emission data.

Sample concentrations were between 10^{-4} and 10^{-5} M, although in some instances adjustments were made to obtain 0.9-1.0 Å at the desired wavelength. Samples were purged with argon for at least 25 min. The lamp profile was taken with excitation and emission monochromators set at 338 nm. Excitation and emission monochromator settings were identical to those used in the fluorescence experiments.

Measurement of Equilibrium Constants. Absorption measurements allowed the determination of the equilibrium constants between naphthol and dimethylbenzylamine (DMBA) using serial dilutions. Equilibrium constants were determined by spectral decomposition of solutions of complexed and uncomplexed naphthols. The spectral decomposition was performed by a leastsquares technique in which the best fit to a spectrum of the mixture was obtained from a linear combination of the spectrum of uncomplexed naphthol and a spectrum of naphthol containing sufficient amine to ensure nearly 100% complexation.

Preparation of 1-[(Dimethylamino)methyl]-2-naphthol (1DMN2).²⁷ To a solution containing 15 mL of 95% ethanol,

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2-naphthol (2.05 g, 14.2 mmol), and 40% dimethylamine (2.03 mL, 16 mmol) was added 0.469 g (14.9 mmol) of paraformaldehyde. The mixture was allowed to stir for 1 h at room temperature. The solvent was removed by rotary evaporation, and the resulting oily solid was dissolved in dichloromethane, washed with water, and extracted with 2×30 mL portions of dichloromethane. The extracts were combined, dried over magnesium sulfate, filtered, concentrated, and dried under reduced pressure for 1 h to give 1-[(dimethylamino)methyl]-2-naphthol (1DMN2) (2.55 g, 12.7 mmol, 85%) as a pink solid (mp 75-76 °C): NMR (CDCl₃, 300 MHz) δ 2.41 (s, 6 H), 4.09 (s, 2 H), 4.80 (s, 1 H), 7.09-7.12 (d, 1 H, J = 8.85 Hz), 7.25-7.31 (dd, 1 H, J = 7.76, 7.14 Hz), 7.40–7.46 (dd, 1 H, J = 7.14, 7.02 Hz), 7.67–7.70 (d,

1 H, J = 8.86 Hz, 7.75–7.77 (d, 1 H, J = 8.24 Hz), 7.80–7.83 (d, 1 H, J = 8.67 Hz). The material was further purified by high-pressure liquid chromatography on a silica gel column using acetone for 15 min followed by 50% acetone-petroleum ether. The product was obtained as a colorless crystalline solid, mp 75-76 °C.

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Registry No. DMBA, 103-83-3; N₂, 135-19-3; N2M, 93-04-9; 1DMN2, 5419-02-3; dimethylamine, 124-40-3; paraformaldehyde, 30525-89-4.

Application of the Medium-Enhanced Barrier Model to the Photoisomerization Dynamics of Substituted Stilbenes in *n*-Alkane Solvents

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Photoisomerization rate constants for trans-4,4'-dimethylstilbene, trans-4,4'-dimethoxystilbene, and trans-4,4'-di(tert-butyl)stilbene in n-alkane solvents are treated with the transition state theory equation (Eyring equation) and the medium-enhanced barrier model, $\Delta H_{obsd}^* = \Delta H_t^* + aE_{\eta}$. The *a* value, a measure of the effect of medium viscosity, increases in the order of stillene, dimethylstilbene, dimethoxystilbene, in contrast to results obtained by applying the power law $k_{obsd} = k_t B / \eta_s^a$. The medium-enhanced activation enthalpies and entropies for photoisomerization of the stilbenes obey the isokinetic relationship, and so do the corresponding viscous flow parameters, in the n-alkane solvent series. These relationships show that the apparent slope from the logarithmic form of the power law plot for *n*-alkane solvents is not equal to -a but is a function of -a. As previously concluded, microviscosity should be used in the power law because when shear viscosity is used the n-alkane series does not behave as a continuous medium with respect to the twisting groups. The results presented further support the conclusion that the intrinsic energy barriers for photoisomerization of stilbene and its derivatives are constant in the *n*-alkane solvent series. The relationship between the potential energy barrier height, the Arrhenius activation energy, and the activation enthalpy is discussed.

Introduction

The photoisomerization of the stilbenes has been studied extensively for several decades.¹ It has been well established that photoisomerization of trans-stilbene by direct excitation proceeds through its excited singlet states.² The initial step of the isomerization is subject to an intrinsic potential energy barrier and corresponds to twisting of planar excited *trans*-stilbene, ¹t*, to a perpendicular state, ¹p*. In supersonic jet expansions, the barrier height for the isolated molecule was determined to be 3.4 ± 0.3 kcal/mol from the excess excitation threshold energy required for radiationless decay (isomerization).³ Alternative values of 2.6^{4a,b} and $3.7 \pm 0.2 \text{ kcal/mol}^{4c,d}$ have been based on the optimal fitting of the RRK and RRKM theories to the excess energy dependence of fluorescence quantum yields and decay rate constants, respectively. The isomerization of stilbene can be viewed as a large-amplitude twisting motion about the central bond. In solution, this motion depends strongly on medium friction. Therefore, trans-stilbene has been used widely^{1c,5-8} as the prototypic system with a high intrinsic energy barrier (>kT) for the study of medium viscosity effects on reaction rate constants, a subject that has been attracting great attention.

A generally applied theoretical model in accounting for medium effects is based on the concept of a Brownian particle escaping over a one-dimensional potential energy barrier that exists in a

potential energy curve that is piecewise parabolic. It gives rise to the Kramers equation^{2c,9} which is derived as an approximate solution to the Langevin equation. The Kramers equation is given by

$$k_{\rm obsd} = (\omega/2\pi)(\beta/2\omega')\{[1 + (2\omega'/\beta)^2]^{1/2} - 1\}e^{-E_0/RT}$$
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