plots are meaningful only for systems exhibiting convergent intercepts.¹ (In almost every case, the flat-band potential obtained by the onset of photopotential was less negative than that determined by capacitance measurements.) The fact that better correspondence of the two methods is observed in the two solvents of lowest dielectric constant is probably coincidental for close correspondence of these values is also observed in water, the medium of highest dielectric constant.

No monotonic variation of linearity in Schottky-Mott plots with solvent dielectric was observed.

The data in Table II compare band positions in acetonitrile for n-SnO₂ polycrystalline electrodes, both in naked and derivatized form. In electrode 4, the attached molecule exhibits redox chemistry only at potentials more negative than $V_{\rm fb}$, but, in electrode 5, the attached molecule should be electroactive in the band-gap region. It is fairly remarkable than that the $V_{\rm fb}$ of these three electrodes should apparently lie so close in energy. Our observation that derivatization causes only minor shifts in band-gap position is consistent with the minor shifts upon derivatization observed by others.¹³⁻¹⁶ Our observed shifts are toward more negative potentials, however, whereas others have observed shifts to less negative potentials.

The slopes of the Schottky-Mott plots from which the data in Table II were derived can also be used to determine donor density. If a value of 24 is used in eq 1 for ϵ (SnO₂),²⁵ we calculate donor densities on the order of 10^{19} , the specific value varying with pretreatment. We note that, if care is not taken to ensure near monolayer coverage by the derivative,¹⁶ i.e., if extensive polymerization occurs

upon derivitization, significant nonlinearity and frequency dispersion is observed in the Schottky-Mott plots and that a large difference between an average x intercept and the onset of photopotential can be observed.

Perhaps the most striking conclusion derivable from our data is the rough similarity of band position in solvents of widely differing physical properties and in naked and derivatized electrodes (3 vs. 4 or 5) irrespective of whether the attached molecule undergoes redox reactions at potentials inside (5) or outside (4) the band gap. Thus, the common assumption that interface energetics are not dramatically altered by derivatization seems justifiable. Caution should be exercised in refraining from overgeneralizing these conclusions though, since larger deviations from ideality and more profound solvent dependence has been observed in less stable, smaller band-gap materials. In these latter materials, Fermi level pinning²⁶ and/or inversion effects^{1,27,28} may complicate observed behavior. Furthermore, quantitative interpretatation of photoelectrochemical results will be strongly affected by even the small band shifts reported here.

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Photophysical Properties of Saturated Amines in Slightly Polar Media. Saturated Ethers

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The fluorescence properties of a prototype saturated amine, N,N-diethylmethylamine (DEMA), were examined in diethyl ether and in tetrahydrofuran (THF). In going from a nonpolar medium (n-hexane) to more polar media (diethyl ether and THF), the fluorescence of DEMA undergoes a substantial red shift (292-308-340 nm), along with a diminution in quantum efficiency and an increase in lifetime. The shift in the fluorescence spectrum occurs continuously as the amount of THF in THF/n-hexane mixed solvents is increased. These observations are discussed within the framework of universal and specific interactions. Consideration is also taken of the change in geometry of DEMA in the ground and excited states, and some properties of a "rigid" amine, 1-azabicyclo[2.2.2]octane, are compared and discussed. The question of specific complexation of the amine excited state with the solvent molecules is raised (amine/ether exciplex), and it is concluded on the basis of the properties of aminoether model compounds that a 1:1 exciplex cannot account for the observed photophysical properties. It seems possible that the original view of Muto, Nakato, and Tsubomura that the ether solvent media stabilize the Rydberg or Rydberg-like excited state of the amines may account satisfactorily for the observations.

Introduction

The fluorescence quantum efficiencies of saturated tertiary amines in the vapor phase^{1,2} and in nonpolar solvents such as saturated hydrocarbons have been shown

to be quite large.^{3,4} For example ϕ_f for triethylamine in n-hexane is 0.69, and this value is typical of many other simple monoamines. Because of the potential exploitation of saturated tertiary amines fluorescence as a probe or an

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 TABLE I: Certain Properties of the Solvents along with Photophysical Characteristics of DEMA and Abco

 in These Solvents

solvent	ε ^a	μ ^b	IP^c	$\tau_{\rm f}$, ns	$\phi_{\mathbf{f}}^{d}$	$k_{\rm Q}, {\rm M}^{-1} {\rm s}^{-1}$	$k_{\rm R}, 10^{7} {\rm s}^{-1}$	$\lambda_{\max}(fluor)^e$
<i>n-</i> hexane diethyl ether THF	$1.89 \\ 4.34 \\ 7.32$	(0) 1.15 1.63	9.73 (9.41) 9.77 (9.38)	26.0 42 48	$0.64 \\ 0.44 \\ 0.14$	6.0 × 10° 1.0	2.4_{6} 1.0 0.29	292 (272) 308 340 (325)

^a Dielectric constant. ^b Dipole moment, D. ^c Vertical IP (adiabatic IP); data taken from ref 18. ^d Based on a value of 0.69 for triethylamine $(1 \times 10^{-4} \text{ M})$ in *n*-hexane. ^e Values in nm for DEMA (Abco).

analytical tool, especially in biological applications which allow the use of ca. 250-nm excitation light, we have examined the fluorescence properties of this fundamental chromophore with the aim of determining the influence of environmental conditions on radiative and nonradiative processes.

The saturated amine represents the interesting situation of a polar molecule which undergoes a radical geometry change in the excited state to a planar or nonpolar configuration. Thus the interaction between the electronically excited amine, which is characterized by its own timedependent dipole moment, with a polar medium is of considerable interest within the context of solute-solvent interactions. Moreover, since the upper states of ammonia and also the saturated amines have been assigned as Rydberg or Rydberg-valence conjugate states centered on the N atom,^{5,6} the question arises as to whether the Rydberg character of the (lowest) excited state is preserved in the condensed phase and, if so, what the consequences of the solvation of the Rydberg state are on the photophysical properties of the amine.

One of the more practical aims of the research was to determine the conditions under which (i.e., the types of solvents) the saturted amines retained their intrinsically high emissivity. The results of a quantitative study of the susceptibility of the amines to fluorescence quenching reactions is reported elsewhere.⁷

Results and Discussion

With the exception of the saturated hydrocarbons, in which saturated amines are highly fluorescent, the only other class of common solvents in which the amines are strongly emissive is saturated ethers.⁸ For example, the quantum efficiencies of N,N-diethylmethylamine (DEMA), which was used as a prototype in this study, in diethyl ether and tetrahydrofuran (THF) are 0.44 and 0.14, respectively. The low concentration-limiting fluorescence lifetimes of DEMA in these solvents are found to be 47 and 44 ns, respectively.

There are also dramatic red shifts in the emission spectra of DEMA in these media relative to *n*-hexane; for example, λ_{max} values are 292, 308, and 340 nm in *n*-hexane, diethyl ether, and THF, respectively. These data are summarized in Table I which also contains some properties of the solvents used. In addition to the progressive red shift which increasing solvent polarity, the DEMA fluorescence spectrum shows considerable broadening as well as the obliteration of the subtle vibronic features which can be discerned in the spectrum in *n*-hexane. These spectra are portrayed in Figure 1 and are consistent with the observations reported by Muto et al.⁹ for 1,4diazabicyclo[2.2.2]octane (Dabco) and by Vanderauweraer



Figure 1. Uncorrected fluorescence spectra of DEMA (10⁻⁴ M) in *n*-hexane (—), diethyl ether (----), and THF (-···). $\lambda_{exc} = 230$ nm.

et al.¹⁰ for triethylamine in similar solvents.

It is important to point out that, while the fluorescence decay curve of DEMA in THF, monitored at 340 nm (λ_{max}), is monoexponential, the decay curve analyzed at 290 nm (which is very near λ_{max} in *n*-hexane solution) exhibits nonexponential decay according to

$$I_{\rm f}(t) = \exp(-t/6) + 2 \exp(-t/40)$$

(where t is in ns) for a 5×10^{-4} M solution. As the solvent medium is made richer in *n*-hexane, the short-lived component is sharply reduced in intensity and slightly lowered in lifetime. For example, in 60% (vol/vol) THF, the decay curve, also analyzed at 290 nm is¹¹

$$I_{\rm f}(t) = \exp(-t/4) + 25 \exp(-t/25)$$

It might be speculated that the fast component observed at 290 nm corresponds to the fluorescence of excited DEMA molecules prior to solvent-solvent relaxation. It would be thus expected that, as a consequence of this process, the emission observed at 340 nm would accordingly exhibit a growing-in time dependence. Upon very careful examination of the fluorescence decay at 340 nm on a much shorter time scale, however, no evidence of a negative component (having a time constant of 6 ns) could be found. Thus, one must conclude that the weak, fast component seen at 290 nm is either due to a solvent impurity (not removed by immediately prior distillation) or to a competitive reorganization process.

In this context, it is noteworthy that Muto et al. reported that the red shift in the fluorescence spectrum of Dabco in THF vanished (vis-a-vis the vapor phase) at 77 K (at which point THF is not fluid).⁹

As the solvent composition is further varied, and eventually becomes pure *n*-hexane, the DEMA fluorescence lifetime and quantum efficiency revert continuously to the respective values observed in the nonpolar medium. Likewise, the emission spectrum of DEMA gradually and continuously shifts from 340 to 292 nm and becomes

⁽⁵⁾ See for example M. B. Robin, "Higher Excited States of Polyatomic Molecules", Vol. I, Academic Press, New York, 1974, pp 23-31.
(6) Reference 5, pp 76-84.

⁽⁷⁾ A. M. Halpern and K. Wryzykowska, J. Photochem., 15, 147 (1981).
(8) The lifetime and quantum efficiency reported are reproducible only in freshly distilled, deaerated THF solutions.

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⁽¹¹⁾ It should be noted that the lifetime of DEMA in pure n-hexane is ca. 23 ns at the amine concentration studied.

narrower. No new, distinct emission system can be discerned and thus exciplex emission is not immediately indicated (vide infra).

In order to account for the observed red shift in the fluorescence spectra of the amines in polar solvents, we can consider two simple general models. Birks, in reviewing the phenomenology of solvent effects on emission and absorption spectra, makes a distinction between universal interactions and specific interactions involving the solute with the solvent medium.¹² In the former case, spectral changes occur as a result of the interaction of the solute with the continuous, bulk properties of the medium (as characterized by the static dielectric constant and the refractive index). According to the latter model, these changes are brought about as a consequence of the formation of stoichiometric complexes between the solute and the solvent molecules. Thus, one model stresses the continuous nature of the solvent environment, while the other focuses upon the molecular properties of the solvent. Both of these models will be applied to the case of the saturated amines in saturated hydrocarbon and saturated ether solvent media.

Universal Interactions

According to this model, the solute interactions with the solvent medium primarily as a result of electrostatic (i.e., ion-dipole, dipole-dipole, etc.) interactions. Thus, the important properties of the system are the dipolar or ionic character of the solute in the Franck-Condon and relaxed ground and upper states and the dielectric properties of the solvent medium. The case of a red shift in the fluorescence spectrum with increasing solvent polarity is interpreted in terms of the differential solvation of the relaxed excited state, which would have a larger dipole moment or ionic character relative to the ground state, assuming that solute-solvent dielectric relaxation is fast compared with the radiative process.

Muto et al.⁹ briefly considered the mechanism by which the large red shift in the amine fluorescence in ether solvents takes place. They were able to account for the ca. 5000-cm⁻¹ red shift in the Dabco spectrum (in THF vis-a-vis *n*-pentane) in terms of a solvated Rydberg state. According to this view, the stabilization of the excited state arises primarily from the ion-dipole interaction between the 3s-Rydberg cationic core and the solvent medium. These authors discounted the roles of dipole-dipole and quadrupole interactions, and further argued that an upper state electronic reorganization (from a σ^* to a 3s-Rydberg state) occurred.

Dabco is, of course, a nonpolar molecule by symmetry, and one would not expect an upper state dipole-dipole mechanism to pertain. For monoamines, however, one must consider the role of the permanent dipole moment in coupling with the polar medium. In order to apply this model to the saturated amines, we must keep in mind two types of relaxed states: the geometrically relaxed state and the solvent relaxed state. This distinction is important because it is reasonable to assume that the geometrically relaxed excited states of the amines are planar, or nearly planar within the limitations imposed by the three alkyl substitutents. It is, presumably, this large geometry change (from pyramidal to planar) which gives rise to the very large Stokes shift, even in the vapor phase and in nonpolar solvents. Thus, for example, the importance of dipoledipole stabilization depends not only on the strength of the excited state dipole (in this case, the Franck-Condon

(FC) state), but also on the superposition of the time dependence of the excited state amine dipole moment with that of the dielectric relaxation of the solvent.

That dipole-dipole stabilization is operant in the amines, at least to some extent, can be seen by comparing the red shifts of DEMA, a "flexible" amine with 1-azabicyclo-[2.2.2]octane (Abco), a "rigid" amine. As indicated in Table I, the red shift in the fluorescence spectrum Abco in THF (vis-a-vis *n*-hexane) is ca. 1200 cm⁻¹ larger than that of DEMA. Comparison with triethylamine results in a ca. 700-cm⁻¹ larger red shift for Abco.

In considering the overall importance of the universal solvent interaction model, both the FC and the relaxed excited states must be taken into account. The interaction between the polar FC state with the solvent medium can arise from dipole-dipole coupling. In order for this situation to prevail, however, the geometry relaxation of the FC state to the planar (or nearly planar) configuration must be slower than (or at most on the same time scale as) the solvent relaxation. This seems to be a rather harsh requirement because the dielectric relaxation time of the solvent is on the order of 10^{-11} - 10^{-12} s, and it would thus imply that the geometry relaxation of the excited amine is slower than this rate. This appears to be too slow for the pyramidal \rightarrow planar transition in an amine (e.g., DEMA) which does not possess sterically bulky substituents.

Interestingly, Halpern and Wong, in discussing the temperature dependence of saturated amine fluorescence intensity, have suggested that the reorganization of the FC excited state to the geometry relaxed state is an activated process.⁴ Nevertheless, it is not an immediately appealing assumption that solvent-solute relaxation can kinetically compete with the solute geometry relaxation, although perhaps the latter process is slowed down by the concerted action of the polar solvent molecules.

The stabilization of the relaxed, or planar, state can arise from two different sources: quadrupole-dipole and iondipole interactions. The importance of the former can be discounted as being intrinsically too weak (bearing extraordinarily close contact between the solute and solvent). The ability to rationalize the degree of excited stabilization in a polar medium in terms of a solvated Rydberg state (i.e., ion-dipole interaction) has been noted above.

Specific Interactions. Possible Role of an Exciplex

As mentioned above, the role of an amine-ether exciplex cannot be immediately dismissed (vide supra). It is possible to rationalize that such an association between an electronically excited (geometrically relaxed) amine and a saturated ether molecule can indeed take place. According to this view, the excited amine has appreciable radical cation character, and thus coordination between the N^{δ +} center with one or possibly two ether molecules, which would act as a Lewis base, would occur.

With this interpretation, the red shift of the amine fluorescence spectrum depends upon both the stability of the exciplex and the degree of repulsion between the ground-state amine-ether partners. These factors, in turn, are sensitive to the electronic and structural properties of the amine and ether molecules. If one presumes that the exciplex stability arises from a charge-transfer mechanism, one would anticipate that the ionization potential (IP) of the donor (the ether molecule) would play an important role. From Table I, is is evident that the IP's of the diethyl ether and THF are very similar.¹³ In fact, the vertical and

⁽¹²⁾ J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, London, 1970, pp, 109–119.

⁽¹³⁾ J. M. Behan and F. M. Dean, Tetrahedron, 32, 167 (1976).

TABLE II:Summary of Photophysical Properties ofAminoethers I and II and Model Compounds

amine	$\lambda_{\max}(\text{fluor}),$ nm	$\tau_{\rm f},$ ns	$\phi_{\mathbf{f}}{}^{a}$	$k_{\rm R}, 10^7 {\rm s}^{-1}$
DEMA	292	26.0	0.64	2.5
I	292	21	0.61	2.9
11	292	22	0.59	2.7
III^{b}	365	26.9	0.63	с
IV	288	23	0.81	3.5

^{*a*} Based on a value of 0.69 for triethylamine $(10^{-4} \text{ M in } n\text{-hexane})$. ^{*b*} Data taken from ref 16. ^{*c*} The fluorescence lifetime reflects the excimeric nature of the 365-nm emission.

adiabatic IP's are slightly reversed with respect to each other. Thus this observation, when taken alone, does not lend credence to the exciplex model. One could always postulate that THF is able to achieve a closer approach to the excited amine vis-a-vis diethyl ether, and that the resultant increase in ground-state repulsion energy causes the larger emission red shift.

In order to test specifically the ability of the amine to photoassociate with the ether, we synthesized two dimethylaminoalkyl ethers: N,N-dimethylamino-3-methoxypropane (I) and 1-(N,N-dimethylamino)-2-(2-tetra-



hydrofuranyl)ethane (II). These compounds represent, respectively, dimethylamino groups which are separated from the methoxy and tetrahydrofuranyl oxygen atoms by a three-carbon-atom linkage. This type of bridge is well-known to be significantly effective in promoting the stabilization of the (intramolecular) photoassociation intermediates (excimers and exciplexes) of the pendant groups.^{14,15} For example, with respect to the amines, the emission spectrum of 1,3-bis(N,N-dimethylamino)propane (III) is almost completely dominated by intramolecular excimer fluorescence.¹⁶ It would be thus expected that if a 1:1 exciplex between the excited amine and the ether were responsible for the red-shift emission spectra in the ether solvents, then compounds I and II would accordingly exhibit such fluorescence emission properties, presuming that geometrical requirements for N-O association are similar to those of N–N interaction in the excimer of III.

The fluorescence spectra and lifetimes of I and II in n-hexane solution are, in fact, quite similar to the respective properties of N,N-dimethyl-n-butylamine (IV). These data for compounds I–IV and DEMA are contained in Table II. Thus, one may rule out, with reasonable certainty, the involvement of a 1:1 amine/ether exciplex as the cause of the altered photophysical properties of the amine in ether solvents.

Higher order exciplexes may, however, be considered; for example, a 2:1 exciplex may be formed having a trigonal bipyramid geometry (the two ether O atoms along an axis perpendicular to the planar trialkyl substituents on the amine). This idea is clearly not supported by the observations of Abco in THF: the red shift (relative to n-hexane) is larger than that for DEMA (see Table I).

It thus seems that the simplest conclusion which can be drawn from these observations is that, indeed, the excited state of the amine is "solvted" by the ether molecules, probably nonstoichiometrically. Both dipole-dipole and ion-dipole polarization interactions can stabilize the amine excited state. The former is less important either because of the weakness of the FC state dipole moment and/or because of the very short lifetime of the dipolar FC state. In the latter case, the cationic N-atom core of the excited amine in the planar, or relaxed, state is stabilized by the polar medium. Alternatively viewed, the negative charge associated with the Rydberg excited state more effectively permeates the solvation shell in those media having larger dielectric constants. If this is, in fact, the case, it would give strong support to the idea that the Rydberg character of the excited amine is substantially preserved (or even enhanced) in the condensed phase.

Experimental Section

Materials. DEMA (Pfalz & Bauer) was distilled over CaH_2 prior to use. THF and diethyl ether were distilled over lithium aluminum hydride immediately before use. The fluorescence lifetime of DEMA was found to drop significantly after the solution aged for more than a few days.

N,N-Dimethylamino-3-methoxypropane (I) was prepared from the corresponding primary amine (Aldrich) by the Leuckart reaction with formic acid and formaldehyde. 1-(N,N-Dimethylamino)-2-(2-tetrahydrofuryl)ethane (II): furan was reacted with *n*-butyllithium in anhydrous THF; the adduct was quenched with 2-dimethylaminoethyl chloride, and 1-dimethylamino-2-(2-furyl)ethane was isolated and then vacuum distilled. II was obtained by reducing the furan derivative with hydrogen/platinum oxide in absolute ethanol. The product was a solid which, after three vacuum sublimations, melted at 113–114 °C; elemental analysis, and the NMR and UV spectra were consistent with a compound having the structure of II.

Fluorescence spectra were obtained by using a conventional d.c. spectrofluorimeter with a deuterium source; fluorescence decay curves were obtained with a time-correlated photon-counting apparatus previously described.¹⁷ The data were analyzed by a reiterative convolution method.

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