SYTHESIS AND SPECTRAL STUDIES OF AMIDES OF 9-ANTHROIC ACID

by

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ABSTRACT

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The fluorescence energy, shape of the fluorescence spectrum, and the fluorescence efficiency of 9-anthramide (9-CONH2) and N,N-diethyl-9-anthramide (9-CONEt2) have been investigated as a function of solvent. For the 9-CONH2, the S1 energy ($\bar{\nu}m$) decreases and the fluorescence spectra become structureless at the polar and nonpolar extremes of the solvent scale. This unusual solvent-dependent fluorescence behavior for 9-CONH2 is explained by a significant geometry change subsequent to excitation, whereby the exocyclic group rotates about the anthracene rings. In contrast, 9-CONEt2 shows solvent-independent behavior. The S1 energy generally remains constant and the fluorescence spectra show well-defined vibrational structure in a wide variety of solvents. It appears that the diethyl substitution has a dramatic effect on the fluorescence properties, inhibiting the rotation that has been proposed for unsubstituted amide, 9-CONH2. This difference in fluorescence behavior appears to correlate with the increased bulkiness and electron-donating ability of the ethyl groups. The fluorescence quantum yield (ϕf) of 9-CONEt2 in aprotic solvents and ethanol does not correlate well with solvent polarity. The ϕf of 9-CONEt2 in these solvents is less than that of methyl-9-anthroate. The data suggest a greater participation of the π,π^* triplet state in activated intersystem crossing for 9-CONEt2 than for the ester.

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INTRODUCTION

The fluorescence and absorption properties of many organic compounds can provide significant qualitative and quantitative information about the molecular geometry of the ground and excited states. An understanding of the basic concepts of the fluorescence process, however, is essential before its usefulness can be realized.

During absorption, a photon of light is absorbed, and the molecule is promoted from the ground electronic singlet state, So, to the lowest excited electronic singlet state, S1. The fluorescence emission process is simply the reverse of excitation. As the fluorescence photon is released, the molecule simultaneously returns to So from S1. Based on this simple explanation, the quantity of energy absorbed might be expected to equal the amount of energy emitted, corresponding to excitation and emission at the same wavelength. This situation, however, is very rare. Fluorescence bands are almost always displaced toward longer wavelengths (lower energies) than the absorption bands.(1)

This phenomenon is the direct result of solvent interactions and nuclear vibrations of the molecule and

can be rationalized according to the Franck-Condon (FC) principle illustrated in Figure 1.(2) The FC principle is summarized by the four steps shown below.

$$S_o \longrightarrow S_1 \qquad \text{I}$$

$$S_1 \rightsquigarrow S_1' \qquad \text{II}$$

$$S_1' \longrightarrow S_o' \qquad \text{III}$$

$$S_o' \rightsquigarrow S_o \qquad \text{IV}$$

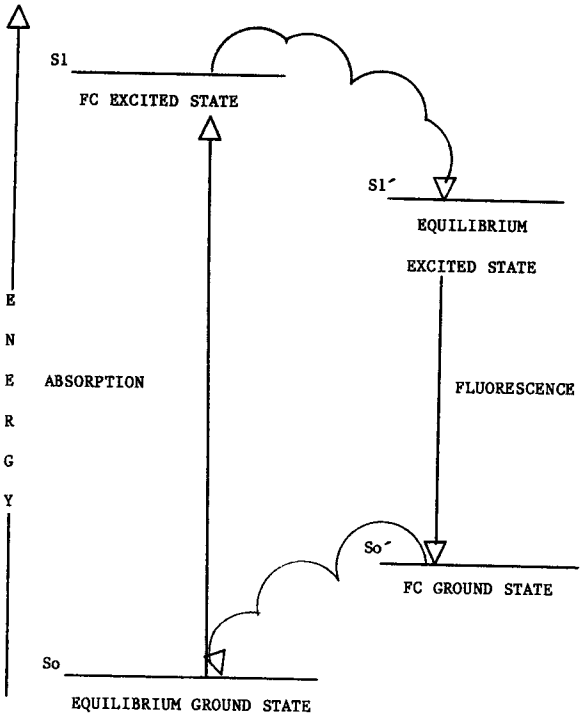
Initially, when a photon of light interacts with a molecule, only the electron distribution changes (I), and the molecular geometry and solvent cage remain in the ground state configuration. This is attributed to the fact that electronic redistribution ($\approx 10^{-15}$ sec.) is much faster than nuclear motion (10^{-13} to 10^{-11} sec.).(2) The initial excited state retains the ground state geometry and solvent cavity and is known as the Franck-Condon excited state. Subsequent to electronic motion, nuclear vibrations procede, and the energy of the solvent cage and geometry is minimized for the excited state level, resulting in the equilibrium excited state (II).

Upon emission of radiation, the reverse process occurs. The electron configuration changes rapidly, resulting in the Franck-Condon ground state (III). Subsequently, the nuclei relax and reorient to conform to the new electron distribution (IV), producing a more stabilized equilibrium ground state.

The Franck-Condon principle rests on the simple

Figure 1

Illustration of the Franck-Condon Principle.


S1
FC EXCITED STATE
S1´
EQUILIBRIUM
EXCITED STATE
E
N
E
R
G
Y
ABSORPTION
FLUORESCENCE
So´
FC GROUND STATE
So
EQUILIBRIUM GROUND STATE

fact that nuclear relaxation and electron motion are two separate processes in time.(1) Consequently, the processes of absorption and fluorescence involve different ground and excited states. Fluorescence occurs from an equilibrium excited state, which is lower in energy than the FC excited state, to the FC ground state which is higher in energy than the equilibrium ground state. Thus, the energy of the electronic state transition is smaller in fluorescence than in absorption, and the 0-0 band for fluorescence often lies toward longer wavelengths. The degree of similarity in vibrational transitions between the FC and equilibrium states determines the extent to which a mirror image relationship exists between absorption and fluorescence spectra.(2) Large gaps between the FC and equilibrium states suggest a geometry change upon excitation, while small gaps indicate little nuclear reorientation as light is absorbed. The FC principle suggests that a large shift in the 0-0 band transition for fluorescence and the absence of a mirror image are indicative of a significant difference in molecular geometry and solvation between the ground and excited states.(2)

For anthracene, the absorption and fluorescence spectra are both highly structured (2), reflecting a restricted number of vibrations for both processes. This observation, along with the small shift of the 0-0 band and the mirror image relationship, is indicative of

minimal geometry change upon excitation of the molecule.(2) The molecule remains in a planar configuration subsequent to absorption of radiation.

By contrast, the spectral behavior of methyl-9-anthroates is quite different.(3) The excitation spectrum is very structured and anthracene-like; however, the emission spectrum is considerably red-shifted and diffuse. Since the lowest energy transition of these meso-substituted anthracenes is on the anthracene molecule (4), the spectral properties of methyl-9-anthroate must reflect a dissimilarity in nuclear geometry between the ground singlet state and the excited singlet state.(3)

In the ground state, the ester group is perpendicular to the anthracene rings, due to steric hinderance with the peri-hydrogens at the 1 and 8 positions. The anthracene-like absorption spectra is expected, since there is no interaction between the 9-substituted ester carbonyl group and the ring. Upon excitation, the ester group approaches coplanarity with the ring. The smearing of the vibrational fine structure is attributed to the greater number of vibrational isomers that can occur in this excited state as a result of rotation. The fluorescence spectra of the excited state vibrational isomers slightly differ from each other, and as they overlap, they produce the observed structureless spectra. A great number of vibrations also

accompanies the more efficient conjugation of the exocyclic ester carbonyl substitiuent with the aromatic ring.(5) This conjugation, known as charge-transfer (5), involves delocalization of electron density from the aromatic ring to the electron-withdrawing ester group. The charge-transfer transition must have such a large stabilizing effect in the first excited singlet state if the sterically hindered rotation is favored.

The solvent polarity and hydrogen-bonding effects on the fluorescence of methyl-9-anthroate also indicate unusual behavior for this molecule that is absent in the fluorescence of the parent hydrocarbon, anthracene, and suggest nuclear reorientation for the esters subsequent to excitation.(6) As solvent polarity is increased for the ester, the fluorescence wavelength maximum and mean frequency shift toward lower energies with the greatest effects being in protic solvents.(6) The shifts in fluorescence maxima and mean frequencies are consistent with the hypothesis of an excited state geometry change for the esters. Since the ester carbonyl group is expected to interact with the ring by charge-transfer after absorption of radiation, the excited singlet state should be more polar than the ground state. The more polar solvents stabilize the polar excited state and, thus, shift the fluorescence to lower energies. In protic solvents, hydrogen-bonding must be an additional effect that shifts the

fluorescence.(6) The ester carbonyl oxygen is also more easily protonated in the excited state (6), which is consistent with excited state rotation. At this time, the solvent dependence of methyl-9-anthroate is rationalized only by an excited state geometry change.(6,7) It should also be noted that meso-substituted carbonyl anthracenes, although they are only weakly fluorescent, also appear to undergo this excited state rotation.(8,9)

The solvent dependence of the fluorescence quantum yield, ϕf for meso-substituted carbonyl anthacene compounds such as 9-anthryl aldehyde and 9-anthryl ketone, has generally been explained in terms of a temperature-dependent activated intersystem crossing (ISC) from the first excited singlet π,π^* state to a low-lying triplet n,π^* state ($S\pi,\pi^* \rightsquigarrow T n,\pi^*$).(10,11) This accepting triplet is assumed to lie above $S\pi,\pi^*$, thereby leading to activated ICS.(12)

The situation for methyl-9-anthraote is thought to be different.(7) As solvent polarity is increased for the ester, the ϕf decreases.(6) This solvent dependence of ϕf is attributed to intersystem crossing.(6) In a study involving the temperature dependence of methyl-9-anthroate fluorescence, a relationship between Of and temperature could not be found.(7) The absence of a correlation between ϕf and temperature suggests that the accepting triplet involved in ISC is not a triplet n,π^*

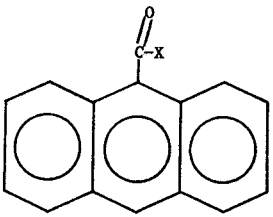
state but more likely a triplet π,π^* state, which lies above the $S\pi,\pi^*$.(7)

This study is concerned with the synthesis and spectral properties of unsubstituted and alkyl-disubstituted amides of 9-anthroic acid. The 9-anthramide and N,N-diethyl-9-anthramide molecules have been synthesized and will be the focus of this study (Figure 2). An attempt has been made to synthesize the N,N-di-isopropyl-9-anthramide but the structure has not been confirmed.

There are two major reasons why these anthracene derivatives have been chosen for analysis. The first reason involves the location of the triplet n,π^* state relative to the first excited singlet state, $S\pi,\pi^*$. Meso-substituted carbonyl anthracenes, such as 9-anthryl aldehyde or 9-anthryl ketone, are weakly fluorescent in almost all solvents. The lack of strong fluorescence is explained by the participation of the low-lying Tn,π^* level in rapid radiationaless intersystem crossing, $S\pi,\pi^* \rightsquigarrow T_n,\pi^*$.(4) According to the El Sayed rule, intersystem crossing between states of different designations, as in the type $S\pi,\pi^* \rightsquigarrow T_n,\pi^*$, is a more allowed process than the forbidden transition between pure states($S\pi,\pi^* \rightsquigarrow T\pi,\pi^*$).(4) By contrast, the meso-substituted carboxyl anthracenes, such as methyl-9-anthroate, exhibit moderate to strong fluorescence. Here, the Tn,π^* level shifts to much

Figure 2

Amidoanthracenes That Have Been Synthesized for this Study



X = NH2 (9-ANTHRAMIDE)

X = N(CH2CH3)2 (N,N-DIETHYL-9-ANTHRAMIDE)

higher energy, making the nonradiative pathway, $S_{\pi,\pi^*} \rightsquigarrow T_{n,\pi^*}$, inefficient and unable to compete with fluorescence. On the carbonyl of 9-substituted amidothracenes, the T_{n,π^*} level lies intermediate to that of the ester carbonyl and the carbonyl group. Since the electronic structure is intermediate to the two anthracene derivatives, the molecular geometry should also be intermediate. Hypothetically, the 9-amidoanthracenes are expected to exhibit intermediate spectral properties relative to these two other anthracene derivatives.

There is a second reason why this study focuses on the spectral behavior of 9-amidoanthracenes. As discussed earlier the unusual fluorescence behavior of anthracene esters such as methyl-9-anthroate has been explained by an excited state geometry change subsequent to excitation.(3) The amide might provide a way to restrict rotation of the carbonyl group relative to the ring. Unlike the ester, the amide group can be disubstituted and, thus, should provide greater steric hinderance with the peri-hydrogens to reorientation. If the steric hinderance is great enough to overcome the resonance-stablizing interaction of the ester carbonyl group with the ring, the amide substituent should remain perpendicular to the anthracene portion upon excitation. The fluorescence spectra would be more structured and anthracene-like compared to that of the ester derivative.

The goal in this study is to examine and evaluate the absorption and fluorescence properties of 9-anthramide and N,N-diethyl-9-anthramide and to see whether the amide group, substituted or unsubstituted, is large and bulky enough to sterically inhibit rotation. The solvent dependence of ϕf, the mean fluorescence enery (energy of S1), and spectral structure will be measured in several solvents that vary in polarity and hydrogen-bond donating and accepting abilities to see if the amides show the same solvent spectral dependence as the esters. These experiments should prove very interesting, since unsubstituted amides have the potential to hydrogen-bond donate and accept, unlike the esters and substituted amides which can only hydrogen-bond accept.

In one study, the protic solvent cage seems to play a significant role in the determination of the molecular geometry of 9-anthramide in water.(13) Sturgeon and Schulman propose that a hydrogen-bond donor solvent cage sterically inhibits excited state rotation of the molecule and prevents conjugation of the exocyclic carbonyl group with the ring upon excitation. It is interesting to note that Sturgeon and Schulman claim that the amide group becomes bound to the protic solvent mostly through the $-NH_2$ group's hydrogen-bond acceptor ability. In aprotic solvents, such as hexane, they report different results. Although the absorption

spectrum is structured, the fluorescence spectrum is highly diffuse and red-shifted in these solvents. It is suggested that the barrier to rotation, the hydrogen-bond donor solvent cavity, is removed in aprotic media, and the amide group is able to reorient to a coplanar state with the ring.(13)

The results of another study by Shon, Cowan and Schmiegel suggest that the fluorescence of 9-anthramide in polar aprotic solvents, such as tetrahydrofuran (THF), is quite structured.(14) Rotation of the amide group is apparently more hindered than in water, but it is not likely to be hindered by a hydrogen-bonded solvent cage since THF has little tendency to form such a cage. Thus, Sturgeon and Schulman's rationale for the water results seem doubtful.

Through the study of the effects of solvation for the 9-amidoanthracenes on ϕf, spectral shifts, mean fluorescence frequency and spectral structure, this investigation will be concerned with the following: (i) confirmation of the proposal for the excited-state rotation for the amide molecules; (ii) determination of the role of the solvent cage in the excited-state geometry of the amides in various interacting solvents; (iii) determination of the role of the low-lying triplet n,π^* states of the amide group in intersystem crossing.

EXPERIMENTAL

CHEMICALS:

The 9-anthramide and N,N-diethyl-9-anthramide were prepared according to methods described in the section entitled Syntheses. Di-isopropyl amine and diethyl amine were Eastman Organic Chemicals. The purity of these amines was confirmed by gas chromatography, which revealed the presence of a single component. The 9-cyanoanthracene was supplied by Aldrich Chemical Company.

Methyl-9-anthroate was synthesized by earlier students. The appearance of superimposed fine structure between 400 and 430 nm in the fluorescence spectrum of the methyl-9-anthroate in absolute ethanol indicated the presence of ester decomposition to the carboxylic acid. Addition of base sharpened the fine structure, confirming the presence of the acid contaminant, since the acid dissociates to the anion in base medium yielding the observed fine structure. To remove the impurities, the ester was stirred in 0.10 M NaOH, filtered and recrystallized from hexane. A fluorescence spectrum at

the highest sensitivity setting of the fluorometer no longer exhibited the fine structure and confirmed the purity of the ester.

The salts, $NaClO_4 \cdot H_2O$ and $MgSO_4 \cdot 7H_2O$, were obtained from the Union College stockroom.

SOLVENTS:

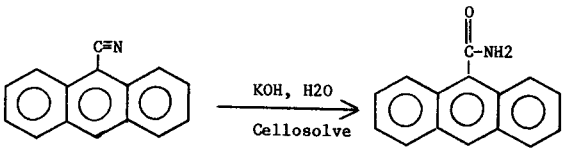
Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile (ACNI) were Matheson Coleman and Bell Spectroquality or Omnisolv solvents. Ethyl acetate (ACNI), p-dioxane (DIOX), hexane (HEX), cyclohexane (CYHEX), methanol (MEOH), and trifluoroethanol (FLET) were obtained from Aldrich Chemical Company. Tetrahydrofuran (THF) was Mallinckrodt analytical grade. Pure grade ethanol (ETOH) was obtained from U.S. Industrial Chemicals. Purification was required for the ethanol and tetrahydrofuran.

Absolute ethanol was distilled from calcium hydride to remove water and then stored in a desiccator to assure dryness.

Tetrahydrofuran was treated to remove both peroxides and water. A 0.5% suspension of cuprous chloride in THF was refluxed for 30 minutes and then distilled to remove trace peroxides. Water was removed by a second distillation from calcium hydride.

SYNTHESES:

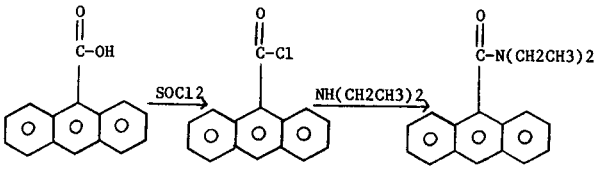
The 9-anthramide was prepared by the method of May and Mosetigg (15) from 9-cyanoanthracene.



When a mixture of 5.0 grams of 9-cyanoanthracene, 4.5 grams of KOH, 3 ml. of H2O, and 20 ml. of ethylene glycol monoethyl ether (Cellosolve) were refluxed for 3 hours, a clear solution resulted which was diluted with 250 ml. of H2O and filtered to give pale yellow precipitate. The precipitate was recrystallized from a 1:1 ethanol:water solution to yield the amide - a pale yellow powder, m.p.= 214-219°C. The yellow amide was recrystallized again, first in a 1:2 water:ethanol mixture and then from benzne. Very pale yellow needles (m.p.= 219-223°C) were obtained and dried overnight in an oven at 100°C; m.p.= 221-222°C (literature m.p.= 219.5°C (1

N,N-diethyl-9-anthramide was synthesized according to the method of Koelsch (16) from 9-anthroic

acid.



When a solution of 1.0 gram of 9-anthroic acid in 8.0 ml. of benzene and 2.0 ml. of thionyl chloride was refluxed for 20 minutes, the solution became clear. Benzene and excess thionyl chloride were removed under a vacuum using the rotary evaporator, and a dark mustard solid remained. This solid was redissolved in 15.0 ml. benzene. As 24.0 ml. of diethylamine were added to the solution, large amounts of diethylammonium chloride evolved as white smoke and precipitate formed immediately. The solution was refluxed for 30 minutes. Benzene and excess amine were removed under vacuum on the rotary evaporator. A dark yellow precipitate was collected and stirred in 0.1 M NaHCO3 for several minutes to remove any unreacted acid. The solid was filtered and washed until the washings were clear. The product was recrystallized from benzene, yielding dark yellow crystals; m.p.= 109.5-111.0°C.

The method of Koelsch (16) was also employed in the attempt to prepare N,N-diethyl-9-anthramide from the acid. The synthesis seems to have been unsuccessful at

this time (see Results). The solid produced decomposed at 146°C.

INSTRUMENTAL:

All melting points were taken on a Mel-Temp melting point appartus.

Absorption measurements were made on either a Cary Model 118C Spectrophotometer or a Beckman D.U. Spectrophotometer.

Uncorrected fluorescence spectra were recorded at room temperature on a Perkin-Elmer Hitachi-MPF-2A Spectrofluorometer interfaced to an Apple computer, using excitation and emission band passes of 7 and 3 nm, respectively. Corrections for photomultiplier and emission monochromator response were performed on the computer as described in the interface manual. (17) Correction capability is available in the region 360-580 nm. Correction factors for the xenon source intensity and excitation monochromator response were determined with a rhodamine B quantum counter.(18)

PROCEDURE:

The fluorescence emission for N,N-diethyl-9-anthramide in hexane, methanol and trifluoroethanol, and for 9-anthramide in all solvents was excited at a wavelength between 360-363 nm corresponding to the peak of the 0-1 band in the absorption spectrum. Since quantum yields were not determined for these samples, the excitation wavelength was less crucial than for those samples for which quantum yields were measured. The excitation wavelenths were chosen where they would not overlap with the emission spectrum. Sample absorbances did not exceed 0.024 at the excitation wavelength.

The fluorescence emission for N,N-diethyl-9-anthramide in dimethylformamide, dimethyl sulfoxide, p-dioxane, ethyl acetate, cyclohexane, acetonitrile, tetrahydrofuran and ethanol was excited at a wavelength between 370-376 nm. This region corresponds to the minimum between the 0-0 and 0-1 band in the absorption spectrum and has a shape similar to that of the reference (methly-9-anthroate in ethanol). In this region the samples and the reference are being excited by nearly equal source intensity which is important for accurate quantum yield determinations. Sample and

reference solutions were prepared in duplicate for quantum yield measurements, and their absorbances did not exceed 0.024 at the excitation wavelength.

Quantum yield determinations were made according to the procedure described by Werner.(19) At room temperature, the fluorescence quantum yield of an unknown fluorophore can be compared to a fluorescence standard by equation 1:

$$\phi u = \frac{\phi r \times Fu \times DFu \times AFu \times Ir \times Ar \times N2u}{Fr \times DFr \times AFr \times Iu \times Au \times N2r} \quad 1$$

where:

ϕ = quantum yield

r = reference

u = unknown

F = area under uncorrected fluorescence spectrum

DF = degassing factor for oxygen quenching

AF = area correction factor

I = xenon source intensity at excitation wavelength

A = absorbance at exciting wavelength

N = solvent refractive index

The reference used in this study was methyl-9-anthroate in ethanol (ϕr= 0.173 (3)) Quantum yields were obtained using equation 1 in conjunction with the computer.(20) Certain variations were also introduced. The area under the corrected fluorescence curve, which was computer calculated (21), was used, so the area correction factor was assigned a value of unity. Relative lamp intensities

at the respective wavelengths of excitation were obtained from the xenon lamp profile. The degassing factors were determined to correct for the quenching of fluorescence by dissolved oxygen. The sample was deoxygenated at least three times by the freeze-thaw degassing method, employing an oil-diffusion pump and reduced pressure. The cell containing the sample solution was removed from the vacuum, and the fluorescence intensity at the wavelength of maximum emission was recorded. The solution was subsequently opened to the air, swirled about and allowed to re-equilibrate with the oxygen in the atmosphere. The intensity at maximum emission was measured on the fluorometer in the same manner as before, with the cell in the exact same position. This measuement was repeated until four measurements agreed within 2% indicating that re-equilibration had been attained. The degassing factor is calculated as the ratio of the uncorrected fluorescence intensity at the maximum emission wavelngth of the deoxygenated sample to that of the oxygenated sample. The degassing factor for the reference, methyl-9-anthroate in ethanol, is 1.13.(3)

The energy of the first excited singlet state, S1, was measured by determining the mean frequency of fluorescence, $\bar{\nu}_m$. A computer program (22) was used to perform the calculation of $\bar{\nu}_m$ according to equation 2:

$$\int_{\bar{\nu}i}^{\bar{\nu}f} F(\bar{\nu})d\bar{\nu} = 2 \int_{\bar{\nu}i}^{\bar{\nu}m} F(\bar{\nu})d\bar{\nu} \qquad 2$$

where $\bar{\nu}i$ is the initial frequency, $\bar{\nu}f$ is the final frequency, $\bar{\nu}m$ is the mean frequency, and $F(\bar{\nu})$ is the corrected fluorescence intensity at a given frequency. The mean wavenumber of fluorescence allows a comparison of S1 energy among molecules with different spectral structure. Mean frequencies were calculated for corrected fluorescence data.

All wavelengths of maximum fluorescence were recorded for corrected spectra (360-580 nm).

In order to see if conformational isomers were present in the ground state of 9-anthramide, the excitation spectra of 9-anthramide were recorded in hexane and in water at two different emission wavelengths. The emission wavelengths were 407 and 490 nm in hexane and 411 and 480 nm in water, corresponding to wavelengths of maximum and minimum emission, respectively.

The hydrogen-bond donor solvent cage for 9-anthramide in water, proposed by Sturgeon and Schulman (13), was checked by measuring the fluorescence spectra of 9-anthramide in pure water and in the presence of structure-breaking salts as $NaClO_4$ and structure-making salts as $MgSO_4$. Three diluted sample solutions were

prepared from a saturated solution of 9-anthramide in deionized water to yield a 5 M $NaClO_4$ solution, a 1.5 M $MgSO_4$ solution, and a water-diluted solution. The predetermined amount of solid salt was added prior to dilution to give known molar salt concentrations and to ensure constant amide concentration after dilution for accurate comparison. Fluorescence emission of all three solutions was excited at the wavelength of maximum absorbance, 362 nm.

Since the fluorescence of the amides is so weak, the contribution of Raman bands from the water to the fluorescence of the amides in water was investigated. The fluorescence emission was measured for the 9-anthramide in water and a pure water sample at an excitation wavelength of 362 nm. The slitwidths and fluorometer settings remained untouched in between the two measurements to assure reproducible conditions.

RESULTS

9-anthramide (9-CONH2) was synthesized by the method of May and Mosetigg.(15) The structure was confirmed by comparison of the observed melting point (m.p.= 221-222°C) with the literature value, 219.5°C (14) and by Infrared spectroscopy (Table 1). There were no distinct peaks for C≡N stretching of a nitrile (2240-2220 cm-1) in the Infrared spectrum, indicating that none of the starting material was present. Thin Layer Chromatography in ethyl acetate and in ethanol confirmed the presence of a single component. An NMR spectrum could not be obtained because the 9-CONH2 was not soluble enough in any of the solvents that were available (chloroform-d, DMSO-d, and acetone-d).

The method of Koelsch (16) was employed to produce N,N-diethyl-9-anthramide (9-CONEt2) from 9-anthroic acid. Its melting point (m.p.= 109.5-111.0°C) could not be confirmed since literature values could not be found. IR and NMR provided sufficient evidence for the correct structure and its purity. Lack of any N-H stretch in the IR spectrum (3100-3400 cm-1) is consistent with a tertiary amide (Table 1). Also, there was no

TABLE 1

Infrared Frequencies of Amidoanthracenes in CDCl3

9-Anthramide

3180 cm-1	moderate	N-H stretching
3350 cm-1	moderate	
1650 cm-1	strong	C=O stretching (amide I band)
1590 cm-1	moderate	NH2 bending (amide II band)

N,N-Diethyl-9-anthramide

2990 cm-1	moderate	aliphatic C-H stretching
3060 cm-1	moderate	aromatic C-H stretching
1620 cm-1	strong	C=O stretching (amide I band)

Product from Synthesis of

N,N-Di-isopropyl-9-anthramide

3420 cm-1	moderate	N-H stretching
3050 cm-1	weak	aromatic C-H stretching
1650 cm-1	strong	C=O stretching (amide I band)

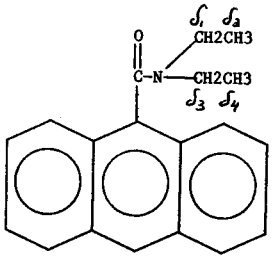
indication of the presence of the carbonyl of the starting acid (1740 cm-1). The NMR spectrum (Table 2) in deuterated acetone clearly verified the purity of the 9-CONH2 and revealed information about the molecular geometry of the diethylamide group that was interesting yet not surprising. As listed in Table 2, there exist two sets of quartets (one for each of the ethyl groups) and two sets of triplets (one for each of the methyl groups). This seemingly abnormal chemical shift difference for the two ethyl groups ($\Delta\delta_{1-3}$= 0.75 ppm) and for the two methyl groups ($\Delta\delta_{2-4}$= 0.70 ppm) can be explained by the amide functional group which places one of the alkyl substituents (-CH2CH3) over the aromatic rings of anthracene. The protons of the ethyl group that are situated above the aromatic rings are very shielded due to the anisotropic effect of the aromatic rings and consequently are shifted upfield. The other ethyl group remains unaffected. The integration data from the NMR spectrum also confirm the structure and purity of the substituted amide (Table 2).

An attempt was made to prepare N,N-di-isopropyl-9-anthramide using the same method of Koelsch (16); however, IR frequencies (Table 1) do not confirm the structure of the molecule. A sharp, strong peak for an N-H stretch occurs at 3420 cm-1. This is inconsistent with the structure of this molecule and suggests the presence of the secondary amide, substituted

TABLE 2

NMR Data for N,N-Diethyl-9-anthramide

(TMS as Standard)



Chemical Shifts of the Methyl Protons	$\Delta\delta_{2-4}$	Chemical Shifts of the Ethyl Protons	$\Delta\delta_{1-3}$
δ_2= 1.00 ppm triplet integration=3	0.70 ppm	δ_1= 3.15 ppm quartet integration=2	0.75 ppm
δ_4= 1.70 ppm triplet integration=3		δ_3= 3.90 ppm quartet integration=2	

by only one isopropyl group. A possible explanation involves an exchange of one of the two isopropyl groups with a hydrogen as a result of the steric hinderance of the isopropyl substituent with the peri-hydrogens on the anthracene molecule.

The Infrared frequency for the carbonyl stretch is observed to be lower in the 9-CONEt2 (1620 cm-1) than in the 9-CONH2 (1650 cm-1) as shown in Table 2.

Tables 3 and 4 summarize the spectral data, frequencies of the 0-0 absorption band ($\bar{\nu}a$), mean fluorescence frequencies ($\bar{\nu}m$), and fluorescence quantum yields (ϕf) of 9-CONEt2 and 9-CONH2, respectively, in several organic solvents. Table 5 contains the Stokes shifts for both amides as measured from the 0-0 absorption band ($\bar{\nu}a$) to the frequency of mean fluoescence ($\bar{\nu}m$). Since the position of the 0-0 absorption band is relatively solvent independent, the Stokes shift will be a useful way to compare shifts in the emission spectra. In each table, the solvents are listed in order of increasing polarity as measured by values of the empirical Dimroth ET(30) solvent polarity scale.(23) The solvents chosen, aprotic and protic, vary over a wide range of polarity. The ϕf and Stokes shifts of methyl-9-anthroate (9-COOMe) are included in Table 5 for comparison.

The absorption spectra of the unsubstituted and substituted amide in all solvents studied are

TABLE 3

Spectral Results for 9-CONET2 in Various Solvents

Solvents	ET(30)[a]	$\bar{\nu}a \times 10^{-4}$, cm-1[b]	$\bar{\nu}m \times 10^{-4}$, cm-1[c]	ϕf[d]
Hexane	31	2.61	2.43	----
Cyclohexane	33	2.60	2.41	0.08
Dioxane	36	2.60	2.40	0.15
Tetrahydrofuran	37	2.60	2.39	0.11
Ethyl Acetate	38	2.61	2.42	0.08
Dimethyl formamide	44	2.59	2.40	0.18
Dimethyl sulfoxide	45	2.58	2.39	0.36
Acetonitrile	46	2.61	2.41	0.09
Ethanol	52	2.61	2.41	0.11
Methanol	56	2.62	2.42	----
Trifluoro-ethanol	61	2.62	2.41	----
Water	63	2.61	2.39	----

[a] kcal/mol; Ref. 18. [b] 0-0 absorption band. [c] Mean fluorescence; +0.01 cm-1. [d] Fluorescence quantum yield; +10% accuracy; +0.1% precision.

TABLE 4

Spectral Results for 9-CONH2 in Various Solvents

Solvents	ET(30)[a]	$\bar{\nu}a \times 10^{-4}$, cm-1[b]	$\bar{\nu}m \times 10^{-4}$, cm-1[c]
Hexane	31	2.63	2.34
Cyclohexane	33	2.62	2.33
Dioxane	36	2.61	2.39
Acetonitrile	46	2.62	2.36
Ethanol	52	2.63	2.34
Methanol	56	2.63	2.34
Trifluoro-ethanol	61	2.64	2.17
Water	63	2.62	2.25

[a] kcal/mol; Ref. 18. [b] 0-0 absorption band. [c] Mean fluorescence; +0.01 cm-1.

TABLE 5

Comparison of Stokes Shifts and Quantum Yields for 9-COOMe, 9-CONEt2 and 9-CONH2

Solvents	9-COOMe		9-CONEt2		9-CONH2
	$\bar{\nu}a-\bar{\nu}m$ x10^{-3}, cm^{-1}[b]	ϕf[f]	$\bar{\nu}a-\bar{\nu}m$ x10^{-3}, cm^{-1}[c]	ϕf[f]	$\bar{\nu}a-\bar{\nu}m$ x10^{-3}, cm^{-1}[c]
Hexane (31)	3.8	----[d]	1.8	----	2.9
Cyclohexane (33)	3.9	0.76[e]	1.9	0.08	2.9
Dioxane (36)	4.6	0.70	2.0	0.15	2.2
Tetrahydrofuran (37)	---	----[d]	2.1	0.11	---
Ethyl Acetate (38)	4.4	0.66[d]	1.9	0.08	---
Dimethyl formamide (44)	4.8	0.70[d]	1.9	0.18	---
Dimethyl sulfoxide (45)	5.0	0.56[d]	1.9	0.36	---
Acetonitrile (46)	4.7	0.39[e]	2.0	0.09	2.6
Ethanol (52)	5.2	0.17[e]	2.0	0.11	2.9
Methanol (56)	5.2	0.11[e]	2.0	----	2.9
Trifluoro-ethanol (61)	6.7	0.02[e]	2.1	----	4.7
Water (63)	---	----	2.2	----	3.7

[a] ET(30) values in parentheses. [b] Stokes shifts calculated from data in Ref. 7 and 22. [c] +0.01 cm-1. [d] Ref. 7. [e] Ref. 3. [f] +10% accuracy.

anthracene-like, possessing absorption frequencies (0-0 absorption band) which show little solvent dependence (Tables 3 and 4).

The fluorescence spectra of 9-CONEt2 in all the solvents have a very structured, anthracene-like appearance. The emission spectrum of 9-CONEt2 in hexane, a nonpolar aprotic solvent, shown in Figure 3, is virtually identical to that in more polar protic solvents, methanol, trifluoroethanol and water, presented in Figures 4,5, and 6, respectively. As solvent polarity increases, there is no apparent change in the spectral structure of this substituted amide. Hydrogen-bonding effects also seem to be insignificant. There is no correlation between the fluorescence energy, as measured by the mean frequency of fluorescence ($\bar{\nu}m$), and solvent polarity (ET(30) values) for 9-CONEt2 (Table 3). The Stokes shift remains approximately constant in the range of solvents studied.

The ϕf of 9-CONEt2 in aprotic solvents (Table 3) also does not correlate well with solvent polarity (ET(30) values). Except for DMSO, the ϕf values fluxuate between 0.08 for cyclohexane (ET(30)= 33) and ethyl acetate (ET(30)= 38) and 0.18 for DMF (ET(30)= 44). In DMSO (ET(30)= 45), the ϕf of 9-CONEt2 is 0.36, while in acetonitrile (ET(30)= 46), a solvent of similar polarity, the ϕf has a very low value of 0.09. Acetonitrile does have some hydrogen-bond donor ability, as reflected by

Figure 3

A Comparison of the Fluorescence Spectra of 9-CONEt2 and 9-CONH2 in Hexane.

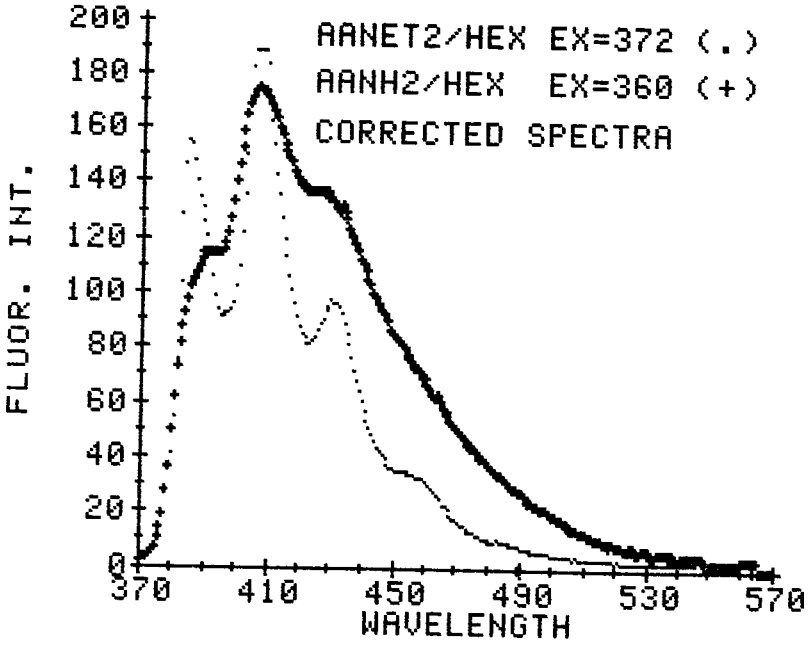

AANET2/HEX EX=372 (.)
AANH2/HEX EX=360 (+)
CORRECTED SPECTRA
FLUOR. INT.
200
180
160
140
120
100
80
60
40
20
0
370
410
450
490
530
570
WAVELENGTH

Figure 4

A Comparison of the Fluorescence Spectra of 9-CONEt2 and 9-CONH2 in Methanol.

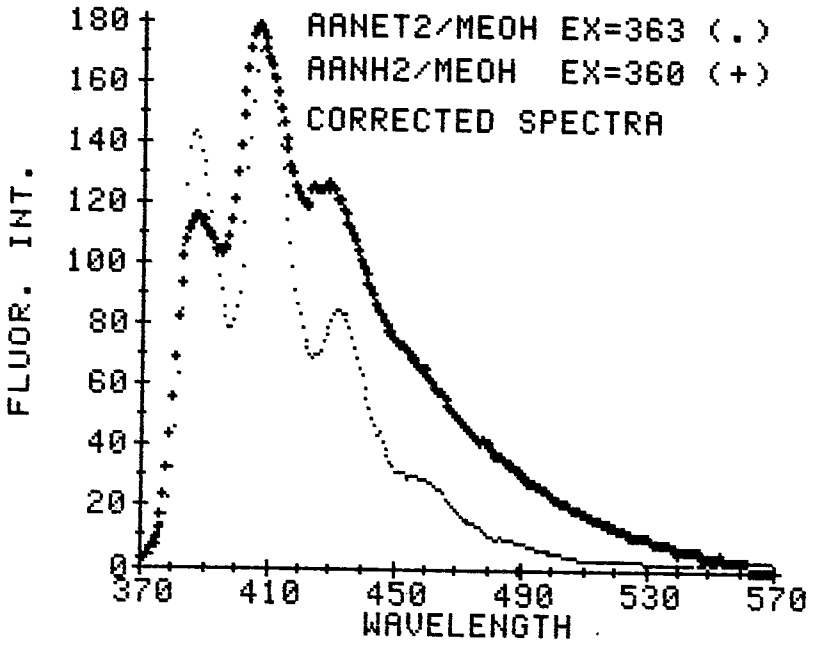

AANET2/MEOH EX=363 (.)
AANH2/MEOH EX=360 (+)
CORRECTED SPECTRA
FLUOR. INT.
180
160
140
120
100
80
60
40
20
0
370
410
450
490
530
570
WAVELENGTH

Figure 5

A Comparison of the Fluorescence Spectra of 9-CONEt2 and 9-CONH2 in Trifluoroethanol.

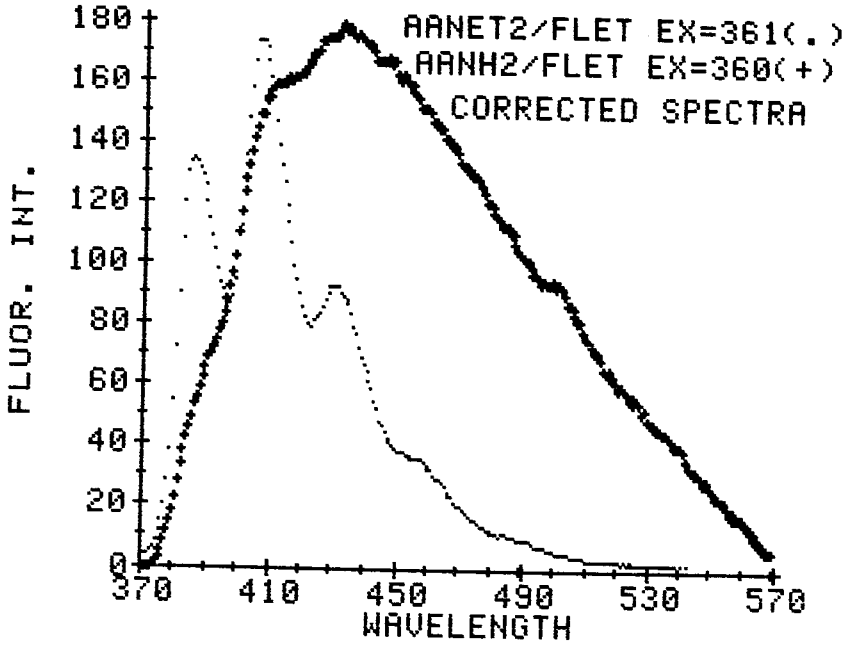
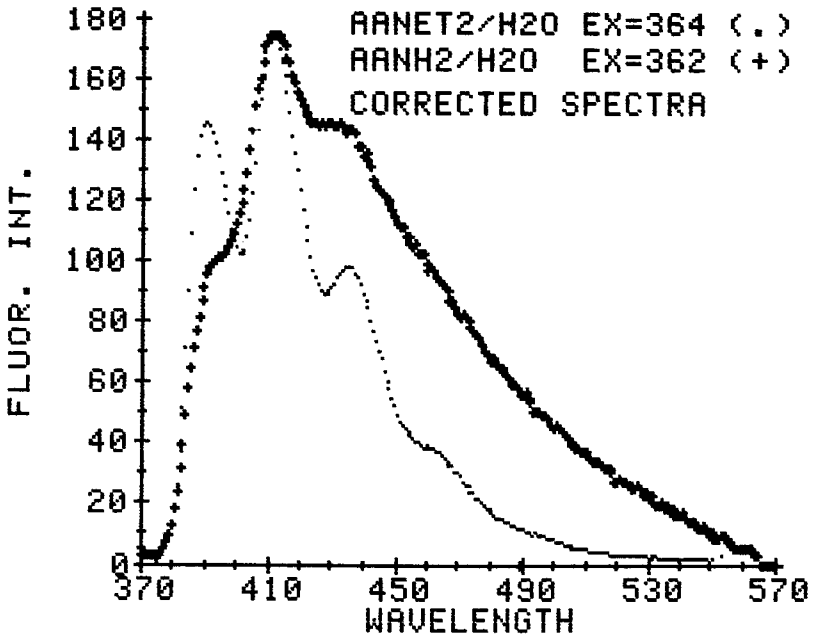

AANET2/FLET EX=361(.)
AANH2/FLET EX=360(+)
CORRECTED SPECTRA
FLUOR. INT.
180
160
140
120
100
80
60
40
20
0
370
410
450
490
530
570
WAVELENGTH

Figure 6

A Comparison of the Fluorescence Spectra of 9-CONEt2 and 9-CONH2 in Water.


AANET2/H2O EX=364 (.)
AANH2/H2O EX=362 (+)
CORRECTED SPECTRA
FLUOR. INT.
180
160
140
120
100
80
60
40
20
0
370
410
450
490
530
570
WAVELENGTH

the Kamlet-Abbaud-Taft hydrogen-bond donating solvent parameter (α= 0.2), but the effect is quite small.(24,25) DMF is a also comparable polar solvent (ET(30)= 44) to DMSO, and yet the ϕf (0.18) of 9-CONEt2 is small relative to the DMSO value.

The ϕf of 9-CONEt2 in ethanol(ϕf= 0.11), a polar aprotic solvent, falls in the range of values for the amide in the aprotic solvents.

The fluorescence spectra of 9-CONH2 are considerably broader and less structured than those of 9-CONEt2 in the same solvents. The fluorescence spectra of these molecules are compared in hexane, methanol, trifluoroethanol and water in Figures 3-6, respectively. Generally, the frequencies of mean fluorescence of 9-CONH2 are red-shifted relative to the fluorescence energies of 9-CONEt2 (Tables 3 and 4). Consequently, the Stokes shifts for 9-CONH2 are larger than those observed for 9-COONEt2 but smaller than 9-COOMe (Table 5).

The fluorescence of 9-CONH2 shows significant solvent dependence. It is evident that the emission of 9-CONH2 is most structured in the intermediate solvent polarity range and becomes red-shifted and more diffuse in solvents at both extremes of the polarity scale. Generally, the effects of structure loss and red-shifting are observed to be greater in the most polar solvents than in the most nonpolar solvents.

9-CONH2 exhibits the most structured emission

in dioxane, followed by acetonitrile, respectively (Figures 7 and 8). As the extremely nonpolar solvents are approached, the emission of 9-CONH2 broadens. Some loss of structure is observed in the fluorescence spectrum of 9-CONH2 in hexane relative to that in dioxane (Figure 7). A similar loss is observed for 9-CONH2 in cyclohexane, another very nonpolar aprotic solvent. The fluorescence energies ($\bar{\nu}m$) of 9-CONH2 in cyclohexane and in hexane are red-shifted by 600 and 500 cm-1, respectively, versus the energy in dioxane. The Stokes shift increases from dioxane(2200 cm-1) to hexane and cyclohexane (2900 cm-1).

As solvent polarity is increased relative to dioxane, the fluorescence of 9-CONH2 again becomes diffuse and shifts to lower energies. The fluorescence of 9-CONH2 in ethanol and methanol are shown in Figures 4 and 5, respectively. The emission bands broaden and the mean frequencies red-shift by approximately 500 cm-1 relative to those in dioxane. In the very polar solvents, trifluoroethanol and water, the fluorescence of 9-CONH2 becomes extremely red-shifted and structureless relative to that in dioxane, an effect not observed for 9-CONH2 in the very nonpolar solvents. The emission spectrum of 9-CONH2 in water exhibits minimum spectral structure (Figure 6), while the fluorescence of the amide in trifluoroethanol experiences a severe loss of all vibrational structure (Figure 5). The fluorescence

Figure 7

A Comparison of the Fluorescence Spectra of 9-CONH2 in Hexane and Dioxane.

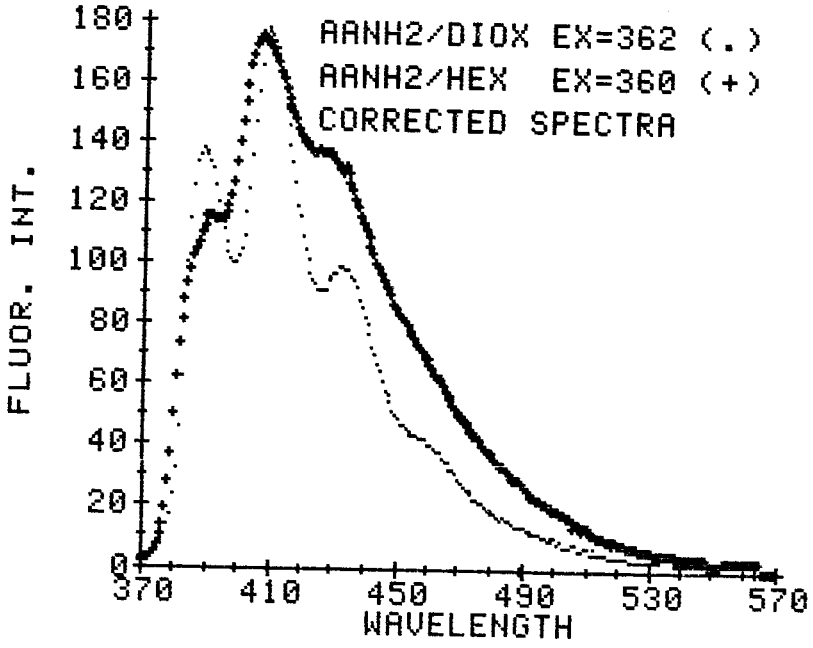
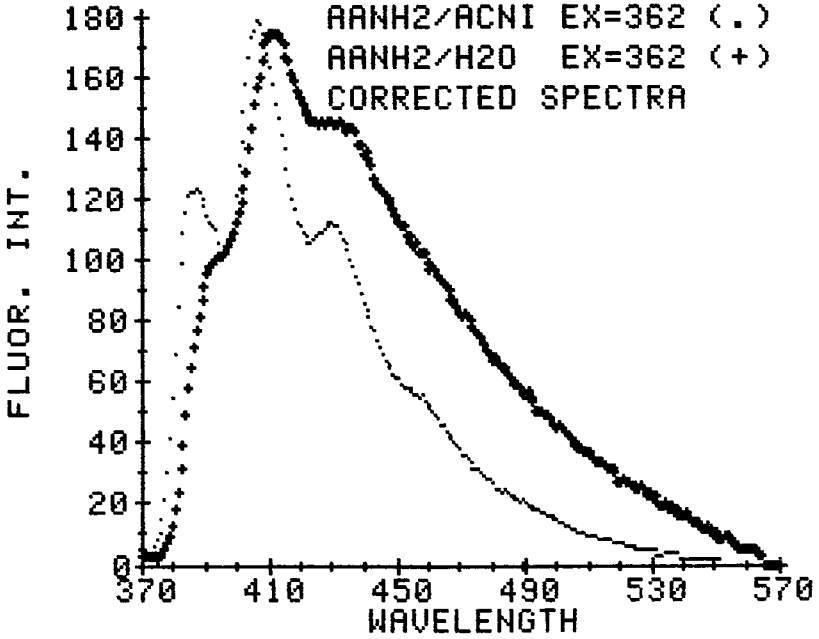

AANH2/DIOX EX=362 (.)
AANH2/HEX EX=360 (+)
CORRECTED SPECTRA
FLUOR. INT.
180
160
140
120
100
80
60
40
20
0
370
410
450
490
530
570
WAVELENGTH

Figure 8

A Comparison of the Fluorescence Spectra of 9-CONH2 in Water and Acetonitrile.


AANH2/ACNI EX=362 (.)
AANH2/H2O EX=362 (+)
CORRECTED SPECTRA
FLUOR. INT.
180
160
140
120
100
80
60
40
20
0
370
410
450
490
530
570
WAVELENGTH

energy ($\bar{\nu}m$) for 9-CONH2 undergoes the greatest red-shifts in water and trifluoroethanol relative to the dioxane energy (1400 cm-1 in water and 2200 cm-1 in trifluoroethanol). Consequently, the Stokes shifts are quite large, increasing from dioxane (2200 cm-1) to water (3700 cm-1) to trifluorethanol (4700 cm-1). Although water (ET(30)= 61) is slightly more polar than trifluoroethanol (ET(30)= 63), the latter (α= 1.61) is a much greater hydrogen-bond donor than water (α=1.07) as reflected by the Kamlet-Abbaud-Taft hydrogen-bond donating solvent parameter.(24,25)

The excitation spectra of 9-COONH2 in hexane and water, using two different emission wavelengths in each solvent, are shown in Figures 9 and 10. The excitation spectra remain structured, anthracene-like, and identical whether the fluoescence emmission occurs at a maximum or at a minimum.

There is no contibution from the Raman bands in water to the emission of the amides in water. The fluorescence spectrum of water did not reveal any emission from water in the region of the spectrum where the amides are being studied.

Table 6 summarizes the spectral data, frequencies of the 0-0 absorption band ($\bar{\nu}m$), mean frequencies of fluorescence ($\bar{\nu}m$) and Stokes shifts ($\bar{\nu}a-\bar{\nu}m$) for 9-COONH2 in deionized water, 5 M NaClO4 and 1.5 M MgSO4. According to Rowland (26), NaClO4 at

Figure 9

A Comparison of the Excitation Spectra of 9-CONH2 in Hexane at Two Different Wavelengths of Emission.

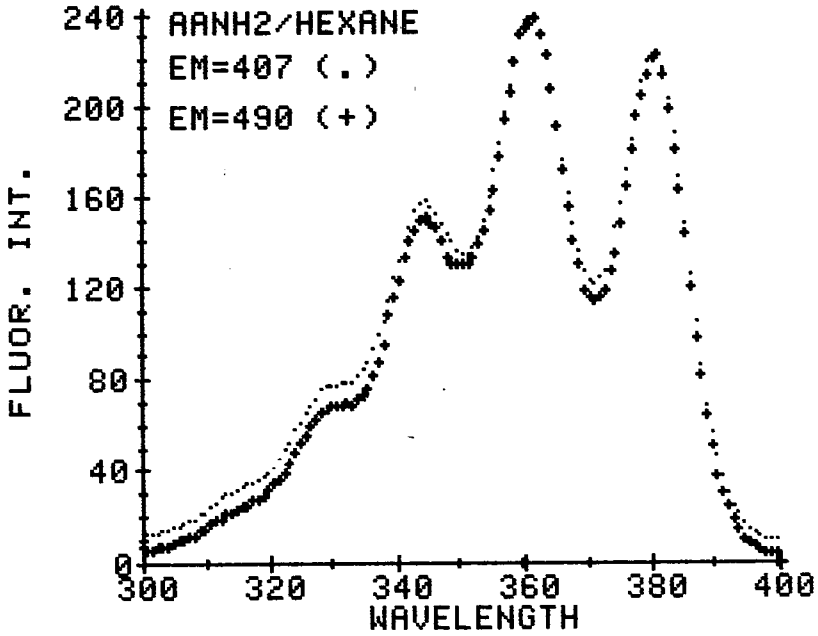

AANH2/HEXANE
EM=407 (.)
EM=490 (+)
FLUOR. INT.
240
200
160
120
80
40
0
300
320
340
360
380
400
WAVELENGTH

Figure 10

A Comparison of the Excitation Spectra of ^{3}-CONH2 in Water at Two Different Wavelengths of Emission.

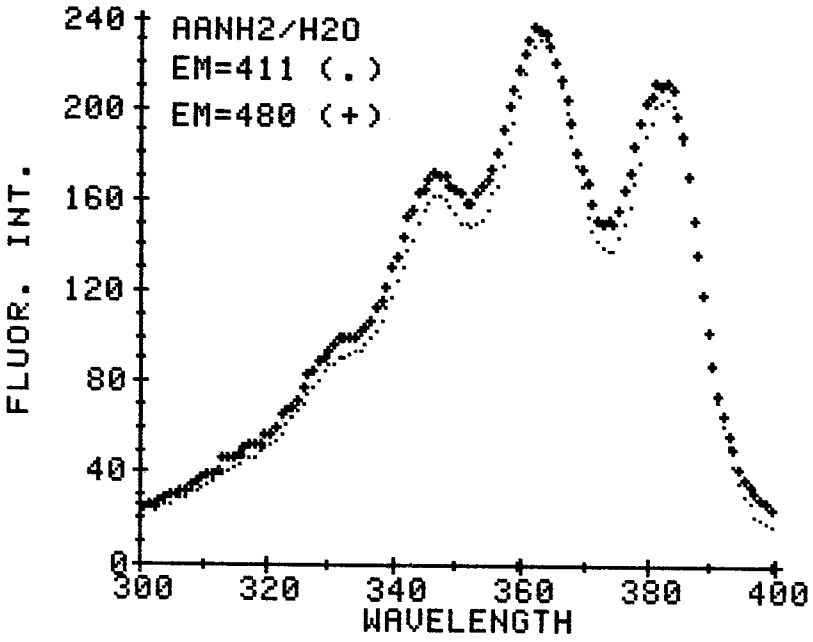

AANH2/H2O
EM=411 (.)
EM=480 (+)
FLUOR. INT.
240
200
160
120
80
40
0
300
320
340
360
380
400
WAVELENGTH

TABLE 6

Fluorescence Data for 9-CONH2 in Water and Salt Solutions

Solution	$\bar{\nu}a \times 10^{-4}$, cm-1 [a]	$\bar{\nu}m \times 10^{-4}$, cm-1 [b]	$\bar{\nu}a-\bar{\nu}m \times 10^{-3}$, cm-1 [c]
Water	2.62	2.25	3.7
5 M NaClO4	2.62	2.23	3.9
1.5 M MgSO4	2.62	2.23	3.9

[a] 0-0 absorption band. [b] Mean fluorescence; [c] +0.01 cm-1. Stokes shift.

TABLE 7

Comparison of the Maximum Fluorescence Wavelength for 9-CONH2

Solvent	Maximum Fluorescence Wavelength (nm) [a]	Maximum Fluorescence Wavelength (nm) [b]
Hexane	407	451
Dioxane	409	440
Acetonitrile	407	448
Ethanol	382	404
Water	411	407

[a] Corrected values from this study. [b] Reference 8.

concentrations greater than 5 M is a strong structure breaker, while MgSO4 is said to be a structure maker.

The absorption spectra of 9-CONH2 in deionized water and the salt solutions are quite structured and anthracene-like. The 0-0 absorption band remains virtually unchanged among the three solutions (Table 6).

No salt effects on fluorescence behavior are observed from one solution to the next (Figures 11-13). There is no shift in excited singlet state energy, as measured by $\bar{\nu}_m$, and thus no change in the Stokes shift (Table 6).

Figure 11

The Fluorescence Spectra of 9-CONH2 in Water.

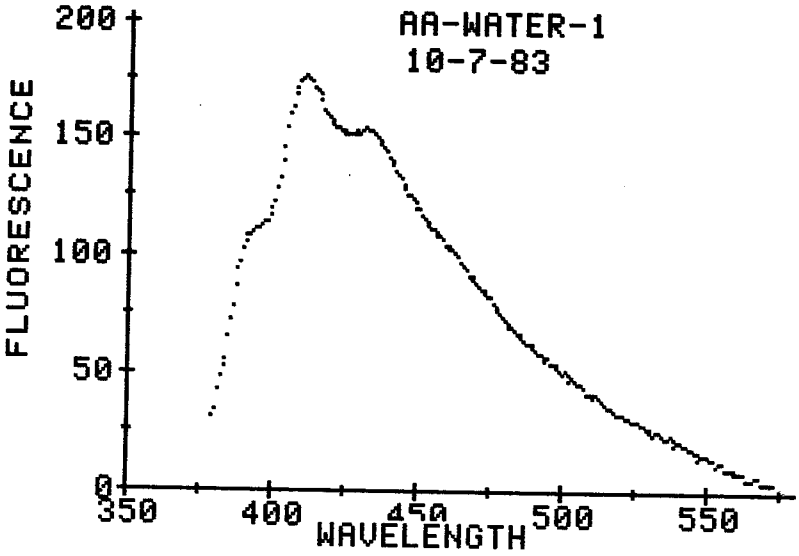

AA-WATER-1
10-7-83
FLUORESCENCE
200
150
100
50
0
350
400
450
500
550
WAVELENGTH

Figure 12

The Fluorescence Spectra of 9-CONH2 in 5 M NaClO4

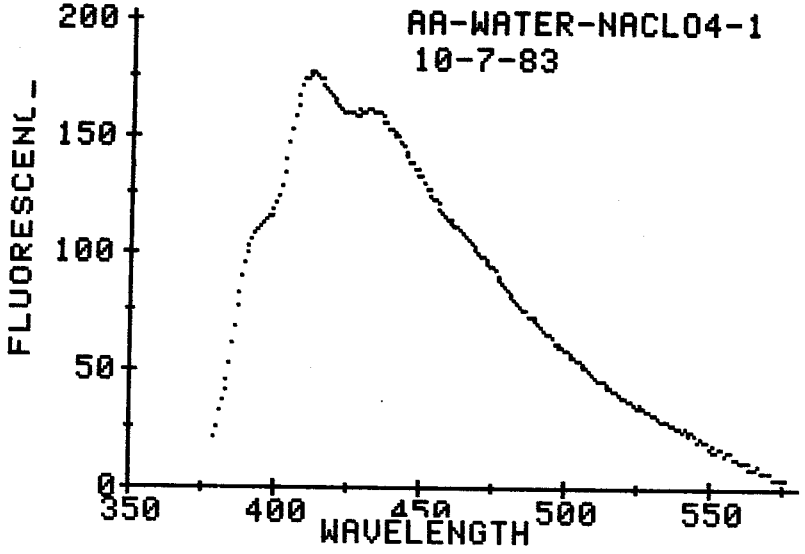
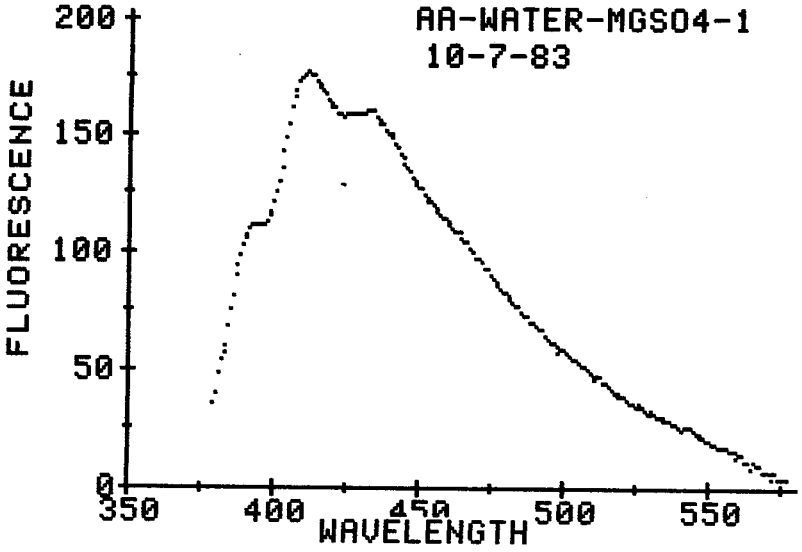

AA-WATER-NACLO4-1
10-7-83
FLUORESCENCE
200
150
100
50
0
350
400
450
500
550
WAVELENGTH

Figure 13

The Fluorescence Spectra of 9-CONH2 in 1.5 M MgSO4


AA-WATER-MGSO4-1
10-7-83
FLUORESCENCE
200
150
100
50
0
350
400
450
500
550
WAVELENGTH

DISCUSSION

In the ground state of 9-CONH2 and 9-CONEt2 in all solvents, steric hindrance to rotation of the carboxamide is observed as reflected by the highly structured absorption spectra. The amide group is perpendicular to the anthracene ring due to the steric hindrance with the peri-hydrogens at the 1 and 8 positions. Due to the nonpolar nature of the ground state, So, the insignificant shift in the 0-0 absorption band with increasing solvent polarity is not surprising. The 9-COOMe in the ground state exhibits similar behavior. (27,28)

The excited state behavior of 9-CONEt2 is quite different from that of the 9-COOMe, as suggested by the absence of solvent polarity dependence of the mean frequency of fluorescence ($\bar{\nu}m$) and Stokes shift. The lowest excited singlet state energy does not change as solvent polarity is increased. The Stokes shifts for 9-CONEt2 are solvent independent in solvents of low ET(30) values as well as in those of high ET(30) values. By contrast, Stokes shifts and solvent polarity (ET(30) values) reasonably correlate for 9-COOMe in the same

solvents.(28) This comparison is illustrated in Figure 14.

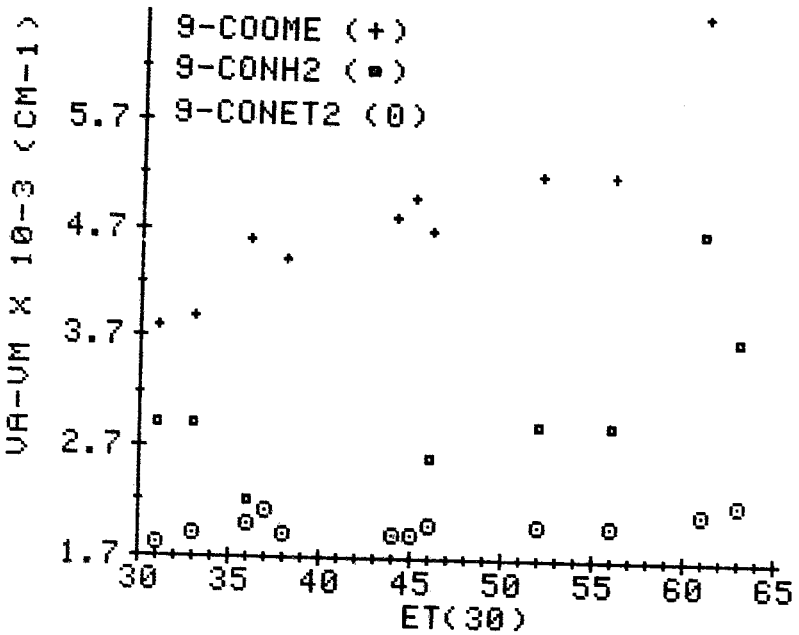
9-COOMe in the excited state in nonpolar solvents shows a stabliizing intramolecular charge-transfer from the anthracene ring to the exocyclic substituent, leading to coplanarity of the ester carbonyl with the ring. This is reflected by the red-shifted, stuctureless fluorescence spectrum.(27) The charge-transfer interaction results in an excited singlet state that is more polar than the ground state. The more polar solvents stablize the polar excited state and thus shift fluorescence to lower energies.

The solvent independence of fluorescence energy and Stokes shift for 9-CONEt2 implies that the excited singlet state, S1, is not much more polar than the ground state. The highly structured fluorescence spectra (Figures 3-6) and relatively constant Stoke shifts for 9-CONEt2 in all solvents suggest that the stablizing conjugation seen between the ester carbonyl and ring for the 9-COOMe does not occur between the amide carbonyl and the ring. The 9-CONEt2 must remain perpendicular to anthracene which indicates that there is no sufficient stablizing effect to favor the sterically hindered rotation upon excitation.

The fluorescence behavior of 9-CONH2 is unique as indicated by the unusual solvent dependence. The fluorescence is greatly Stoke shifted in solvents of very

Figure 14

The Stokes Shift of 9-COOMe, 9-CONH2, and 9-CONEt2 as a Function of ET(30) Values in Several Solvents.


9-COOME (+)
9-CONH2 (▪)
9-CONET2 (0)
VA-VM X 10-3 (CM-1)
5.7
4.7
3.7
2.7
1.7
30
35
40
45
50
55
60
65
ET(30)

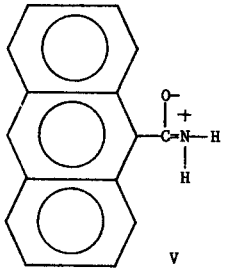
low and very high polarity (ET(30) values) as compared to those of intermediate polarity, with the greatest effects observed at the polar extremes. The dependence is shown in Figure 14.

As shown in Figures 7, the emission of 9-CONH2 becomes broader and less structured in hexane as compared to that in dioxane. The reduction in spectral structure for the 9-CONH2 in nonpolar aprotic solvents suggests rotation of the carboxamide in the excited state into a position approaching coplanarity with the anthracene ring. Lack of strong ground state solvation of the amide group may allow rotation, resulting in the stablizng conjugation between the amide and the ring.

The more structured and anthracene-like fluorescence of 9-CONH2 in dioxane and acetonirile (Figures 7 and 8) indicates that the rotation of the amide group about the ring is somewhat restricted upon excitation in these solvents. These more polar aprotic solvents stabilize the ground state orientation against excited state rotation. Dioxane may hydrogen-bond accept through one of its oxygens and thus sterically inhibit any reorientation. Acetonitrile may also accept a hydrogen from the amide through its nitrogen. Since it is more polar than dioxane, acetonitrile may also provide stablization of the ground state geometry by dipole-dipole interaction.

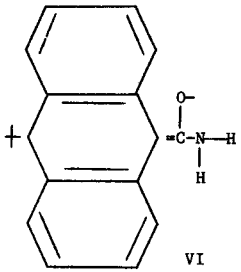
Red-shifted, diffuse fluorescence spectra are

observed for 9-CONH2 in the more polar, protic solvents. This excited state behavior is attributed to geometry differences between So and Sl of 9-CONH2 and to charge-transfer character of the Sl state. The spectral smearing and shift of fluorescence to lower energies increase from methanol (Figure 4) to water (Figure 6). Rotation of the amide group of 9-CONH2 to coplanarity with the ring must become more probable in water. This may result because a hydrogen from the water ties up the free electron pair on the amide nitrogen and subsequently inhibits the amide resonance effect shown as V,



V

where the nitrogen competes with the ring for resonance to the carbonyl group. Fluorescence energy ($\bar{\nu}m$) severely red-shifts since the water is able to stablize the predominant polar excited state shown in VI.

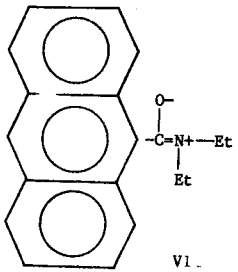


VI

The emission of 9-CONH2 in trifluoroethanol, shown in Figure 5, supports the excited state form, VI, where the resonance interaction predominates between the carbonyl and the ring, allowing rotation. Although water (ET(30)= 61) is a more polar solvent than trifluoroethanol (ET(30)= 63), the trifluoroethanol has much better hydrogen bond donor abilities and more efficiently ties up the electron density about the nitrogen, blocking resonance of the -NH2 group to the carbonyl.

Explanations for the excited state behavior of 9-CONEt2 and 9-CONH2 become clearer upon comparison. There are two effects that contribute to inhibited rotation of the 9-CONEt2 upon excitation. The lack of any solvent dependence of 9-CONEt2, as opposed to the unique solvent dependence of 9-CONH2, implies that the bulkiness of the ethyl groups provides great steric hindrance with the peri-hydrogens to reorientation upon

excitation. In addition, the role of the bulky ethyl groups enhances the electron donating character of the ethyl groups, which results in significant resonance of the -NH2 group with the carbonyl. The Infrared spectrum (Table 1) shows that the carbonyl of 9-CONEt2 stretches at lower frequencies (1620 cm-1) than that of the 9-CONH2 1650 cm-1). These data confirm the enhanced amide resonance effect in the 9-CONEt2 over that in the unsubstituted amide. The ethyl groups electron donate toward the carbonyl group. The resonance effect increases the carbonyl bond length and reduces the frequency of absorption. Consequently, VII is a stronger competitor with VI than is V, thereby reducing ring-carbonyl conjugation in the excited state.



VI

The amide resonance effect for 9-CONEt2 is more significant than the charge-transfer between the carbonyl and the anthracene ring. Even in the very polar protic solvents, water and trifluoroethanol, the emission remains quite structured and anthacene-like (Figures 5

and 6). Solvent hydrogen-bond donation is not sufficient to overcome the enhanced electron-donating ability of the -NEt2 group and the increased steric effect of the two ethyl groups. The protons are unable to compete for the nitrogen electrons with the enhanced amide resonance effect due to the combination of the sterics and the effect itself.

The explanation, that was mentioned previously, for the unusual fluorescence behavior of 9-CONH2 is now understandable. The 9-CONH2 lacks the bulky amide substituents and the enhanced amide resonance that is present in 9-CONEt2. The fluorescence of 9-CONH2 is much less structured than that of 9-CONEt2 in the same solvents. In the very polar solvents, such as water, reorientation of the amide to a planar position is facilitated by the hydrogen-bond donor ability and polarity of the solvent. The completely structureless spectrum of 9-CONH2 in triflouroethanol (Figure 5), as compared to the more structured one in ethanol or methanol (Figure 4), supports the resonance form, II, of 9-CONH2 in the excited state. As the hydrogen bond donor ability of the solvent increases, the ability of the hydrogen to tie up the nitrogen electrons increases. This prevents the amide resonance effect that is seen for the 9-CONEt2, and rotation occurs through the conjugative interaction between the ring and the carbonyl.

Sturgeon and Schulman have also investigated

the fluorescence properties of 9-CONH2 in a few solvents.(13) They find the emission spectra to be completely structureless in hexane but slightly strucured in water and ethanol. They find that the fluorescence maximum in hexane (451 nm) red-shifts more than that in water (407 nm) and ethanol (404 nm). Based on their data, Sturgeon and Schulman propose that the excited state reorientation of the amide group of 9-CONH2 occurs in aprotic solvents; however, in protic solvents like water and ethanol, they suggest that a hydrogen-bond donor solvent cage sterically inhibits excited state rotation and prevents conjugation of the exocyclic carboxamide with the ring.(13)

The effect of the solvent cage on the rotation of 9-CONH2 is not supported by the experiments in this study. It is readily apparent in Table 6 and Figures 11-13, that there are no differences in the spectral behavior of 9-CONH2 in pure water and the salt solutions. According to Rowland (26), the ability of water to hydrogen-bond donate and form tightly bound solvent cages can be altered by the addition of certain inorganic salts. Since the addition of NaClO4 and MgSO4 did not affect the mean frequency of fluorescence or the spectral structure of fluorescence of 9-CONH2 in water, it is concluded that the protic solvent cage plays an insignificant role in the determination of the molecular geometry of 9-CONH2 in the excited state.

Sturgeon and Schulman also observe that the emission of 9-CONH2 in water red-shifts and becomes completely structureless at low pH's as the amide group is protonated at the nitrogen.(13) They infer, however, that the protonation removes the effect of the hydrogen-bonded solvent cage and subsequently allows rotation. An alternative explanation, that supports the results in this study, is that the protonation of the -NH2 group blocks its ability to conjugate to the carbonyl. Consequently, conjugation between the carbonyl and the ring becomes the stablizing factor upon excitation, resulting in rotation. The spectral data for 9-CONH2 in trifluoroethanol in this study confirms this reasoning rather than the theory of Sturgeon and Schulman.(13) The fluorescence of 9-CONH2 is completely structureless in trifluoroethanol, a strong hydrogen-bond donor solvent but one with minimal solvent structuring capability.(28) Thus, a solvent cage that could inhibit excited state rotation is not likely. Rather, a hydrogen that ties up the free electrons on the nitrogen and enhances interaction between the carbonyl and the ring, resulting in rotation is more plausible.

The results in this study are also supported by those in the study by Shon, Cowan and Schmiegel.(14) They determine the emission of 9-CONH2 to be fairly structured in polar aprotic solvents as tetrahydrofuran (THF). The hindered rotation of the amide of 9-CONH2

cannot be attributed to a hydrogen-bond donor solvent cage in this aprotic solvent. THF (ET(30)= 37) is similar in polarity to ethyl acetate (ET(30)= 38), and thus the hindered rotation may be the result of dipole-dipole interaction or hydrogen-bonding donation to the solvent.

The ϕf for 9-CONEt2 in aprotic solvents and in ethanol is determined to be independent of solvent polarity. A decrease in ϕf is observed for the 9CONEt2 upon comparison with those for 9-COOMe. This is attributed to a greater participation of the T_{π,π^*} level in activated intersystem crossing (ISC), $S_{\pi,\pi^*} \rightsquigarrow T_{\pi,\pi^*}$ for 9CONEt2 than for 9-COOMe. Werner has proposed an activated ICS from the S_{π,π^*} to the T_{π,π^*} above to account for the inverse solvent dependence of ϕf for 9-COOMe.(7) In 9-CONEt2, the same ISC is probable but now competes more effectively with fluorescence.

From the mean frequency fo fluorescency, $\bar{\nu}_m$ (Table 3 and Ref. 27), S1 of 9-CONEt2 is about 2000-4000 cm-1 higher in energy than S1 of 9-COOMe. Assuming the shift in T_{π,π^*} to be much less than this, the gap between S_{π,π^*} and T_{π,π^*} is much smaller than that for 9-COOMe. Intersystem crossing to T_{π,π^*} from S1 will require less activation energy than in the case of 9-COOMe and consequently will compete more efficiently with fluorescence, resulting in smaller quantum yields.

It is concluded that the T_{n,π^*} level of

9-CONEt2 does not participate in the ISC that is evident for 9-anthryl aldehyde and 9-anthryl ketone. It is likely that the T_{n,π^*} state is located at much higher energies relative to S1, making the process, $S_{\pi,\pi^*} \rightsquigarrow T_{n,\pi^*}$ unfavorable energetically. If the T_{n,π^*} level was involved, the 9-CONEt2 would be virtually non-fluorescent ($\phi f \cong 0$) like 9-anthryl aldehyde and 9-anthryl ketone. Crossing from S_{π,π^*} to T_{n,π^*} is more allowed than crossing to T_{π,π^*}, and, thus, its presence would be observed as a severe decrease in ϕf values for 9-CONEt2 relative to those for 9-COOMe. The ϕf values for 9-CONEt2 are only slightly smaller compared to those for 9-COOMe. In ethanol, the ϕf for 9-CONEt2 ($\phi f = 0.11$) and for 9-COOMe ($\phi f = 0.17$) are similar. In dioxane, there is only a three-fold decrease for the ϕf of 9-CONEt2 ($\phi f = 0.15$) as compared to that of 9-COOMe.

It is difficult to explain the high ϕf for 9-CONEt2 in DMSO ($\phi f = 0.36$; ET(30) = 45) relative to that in other polar aprotic solvents, as DMF ($\phi f = 0.18$; ET(30) = 44) and acetonitrile ($\phi f = 0.08$; ET(30) = 46). If the large ϕf in DMSO indicates a blue shift of the T_{π,π^*}, resulting in less efficient intersystem crossing, then the Of should be even higher in polar protic solvents such as ethanol. This is not evident. The ϕf of 9-CONEt2 in ethanol is small ($\phi f = 0.11$).

Quantum yields have not yet been determined for 9-CONH2 in this study; however, Schon, Cowan and Schmiegel have investigated fluorescence behavior of 9-CONH2 in benzene, ethanol and THF.(14) They find the expected inverse relationship between the Stokes shifts and the nonradiative rate constant, implying intersystem crossing to $T\pi,\pi^*$ as the major nonradiative decay. The nonradiative constant for 9-COONH2 is reported to decrease from DMSO to ethanol to benzene.(14) As the S1 state lowers in energy to a level below $T\pi,\pi^*$ (increase in Stokes shift), the competing intersystem crossing must decrease (decrease in non-radiative constant). The reduction in the intersystem crossing decay should be reflected by an increase in the ϕf. Schon, Cowan and Schmiegel find that the ϕf of 9-CONH2 does increase from ethanol (ϕf= 0.100) to benzene (ϕf= 0.172); however, the ϕf of 9-CONH2 in THF, where intersystem crossing appears to be greatest, has a very high value of 0.353.(14). As with the large ϕf of 9-CONEt2 in DMSO, this high ϕf of 9-CONH2 in THF is not completely understood. The high ϕf of the two amides in these similar solvents cannot be not attributed to the amide substituent. Other effects must be operative.

REFERENCES:

(1) Stephen G. Schulman, Fluorescence News, 6, 1 (1972).

(2) T.C. Werner, in E.L. Wehry (ed.), Modern Fluorescence Spectroscopy, Vol. 2, Plenum, New York, 1976, Chapter 7.

(3) T.C.Werner, et. al., The Journal of Physical Chemistry, 80, 533 (1976).

(4) Satoshi Hiraymama, J. Chem. Soc., Faraday. Trans., 78, 2411 (1982).

(5) Stephen G. Schulman and W. Larry Paul, Fluorescence News, 1, 25 (1973).

(6) T.C. Werner and Ronald M. Hoffman, The Journal of Physical Chemistry, 77, 1611 (1973).

(7) T.C.Werner and David B. Lyon, Journal of Photochemistry, 18, 355 (1982).

(8) T. Matsumoto, M. Sato and S Hirayama, Chemical Physics Letter, 27, 237 (1974).

(9) S. Hirayama, Bulletin of the Chemical Society of Japan, 48, 1127 (1974).

(10) T.C. Werner, et. al., The Journal of Physical Chemistry, 82, 298 (1978).

(11) K. Hamanoue, S. Hirayama, T. Nakayama and H. Teraniski, The Journal of Physical Chemical, 84, 2074 (1980); as referred to in Reference 7.

(12) G. Gillispie and E.C. Lim, Chem. Phys. Lett., 63, 355 (1979).

(13) Roy S. Sturgeon and Stephen G. Schulman, Journal of Pharmaceutical Sciences, 65, 1833 (1976).

(14) Rita Shao-Lin Shon, Dwaine O. Cowan and Walter W. Schmelgel, The Journal of Physical Chemistry, 79, 2087 (1975).

(15) Everette L. May and Erich Mosetigg, J. Am. Chem. Soc., 70, 1077 (1948).

(16) C.F. Koelsch, J. Org. Chem., 26, 1003 (1961).

(17) T.C. Werner, User's Manual for the Apple/MPF-2A Interface, Flour. Corrector (1983).

(18) R.F. Chen, Anal. Biochem., 20, 339 (1967); as referred to in Reference 3.

(19) T.C. Werner, Revised Procedure for Of Determinations, (7/24/79).

(20) Reference 17, Quantum Yield.

(21) Reference 17, Integrator.

(22) Reference 17, Wvlngth. to Wvnbr. Conversion.

(23) E. Kowsower, An Intoduction to Physical Organic Chemistry, Wiley, New York (1968); as referred to in Reference 27.

(24) M.J. Kamlet and R.W. Taft, J. Chem. Soc., Perkin. Trans., 2, 349 (1979).

(25) O.W. Kolling, Anal. Chem., 53, 54 (1981); as referred to in Reference 27.

(26) Stanley P. Rowland, Water in Polymers, American Chemical Society, Washington, D.C. (1980).

(27) T.C. Werner and Ronald M. Hoffman, The Journal of Physical Chemistry, 77, 1611 (1973).

(28) T.C. Werner and David B. Lyon, The Journal of Physical Chemistry, 86, 933 (1982).