6-1989

The Effects of Hydrogen Bonding on the Spectral Properties of 2'-Acetonaphthone

Kristine A. LoParo
Union College - Schenectady, NY

THE EFFECTS OF HYDROGEN BONDING
ON THE SPECTRAL PROPERTIES OF
2'-ACETONAPHTHONE

by

Kristine A. LoParo

****

Submitted in Partial Fulfillment
of the Requirements for
Honors in the Department of Chemistry

UNION COLLEGE

June 1989

ABSTRACT

LOPARO, KRISTINE The Effects of Hydrogen Bonding on the Spectral Properties of 2'-Acetonaphthone. Department of Chemistry, Union College, Schenectady, New York 12308. June 1989.

The effects of hydrogen bonding on the luminescent properties of 2'-acetonaphthone (2-AN) have been studied. Solvents of varying hydrogen bond donor abilities such as perfluorohexane(PFH), cyclohexane, ethanol, methanol, water, trifluoroethanol(TFE), and hexafluoroisopropanol(HFIP) have been used. An attempt is made to find a relationship between solvent hydrogen bond donor ability, the energy and efficiency of fluorescence emission and changes in 2-AN electronic absorption in these solvents.

The 2-AN spectral properties have also been studied in mixed solvent systems where the molecule is dissolved in a nonpolar solvent, either PFH of cyclohexane, and one of the fluorinated alcohols (TFE or HFIP) is added to see how the spectrum of the solution is altered. The addition of these hydrogen bonding alcohols results in the formation of a 2-AN/alcohol complex. This complex causes a new electronic absorption band to appear in these solutions. Using the Benesi-Hildebrand equation, equilibrium constants can be calculated for the complex formation in the ground state.

The presence of weak hydrogen bonders such as ethanol or propanol are observed to quench the fluorescence emission of 2-AN in a polar solvent and blue shift the maximum.

ii

I would like to dedicate this to my grandmother

Rosemarie Lavorgna LoParo

-may I touch others as she has touched my life

ACKNOWLEDGEMENTS

I would like to extend sincere thanks to Thomas C. Werner for all the time and patience he has contributed to the success of my research project.

Also, I would like to thank Robert Schaefer for his invaluable advice as my faculty advisor. His guidance has helped to pave the pathway of my future.

Many thanks to Christie Sorum, John Marincola and Mark Toher for introducing me to the world of classical studies so that I might broaden my academic horizons beyond the sciences.

Thanks to all of the Senior Chemistry Majors who have provided a friendly atmosphere in which I have developed many important friendships.

Special thanks to the many friends who have supported me through my years at Union College. In particular, Kathy, Lorri, Diane, Ed, and Josh for keeping me sane through the many sleepless nights at Union. Also, thanks to Martin whose friendship has made me happier than I imagined I could be.

Lastly, but most importantly, love and thanks to my parents who have supported me not only financially but emotionally. There are no words which can possibly express the unending gratitude I feel for everything they have given me.

TABLE OF CONTENTS

v

TABLE OF FIGURES

vi

vii

TABLE OF TABLES

INTRODUCTION

The energy level where a molecule is most stable is referred to as the ground state. A molecule will absorb light of a particular frequency which increases its energy to that of an excited state. Following excitation, it will descend to the ground state, losing its excess energy as light or heat. Fluorescence is the process when light is emitted from an excited molecule. A Jablonski diagram illustrates these processes where S_0 is the ground state energy level and S_x (x=1,2...) represents the higher energy singlet states. (Figure 1) Absorption may excite the molecule to a energy level higher than the first. Since all fluorescence normally occurs from the first excited level, the molecule must drop from the higher energy state to the first energy level via a radiationless process known as internal conversion. Internal conversion can also occur to the ground state from the first energy level, thereby competing with fluorescence for the excited-state molecule.

Another radiationless process which competes with fluorescence is intersystem crossing which occurs when the excited electron flips spin direction, and the molecule changes from the singlet to the triplet state. The excited molecule initially exists in a singlet state with all electron spins paired. In the triplet, however, the excited electron changes spin direction, so that two of the electrons are now unpaired. The electrons maintain an optimum distance apart which decreases the electron-electron repulsion, accounting for the lower energy of the

FIGURE 1

Jablonski Diagram

FIGURE 1
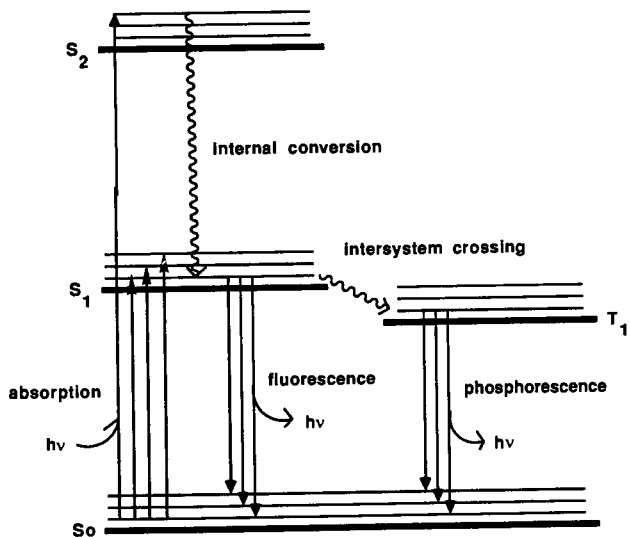
triplet state. When the triplet state molecule emits light, the molecule is said to phosphoresce.

Our study is concerned with fluorescence which will only be observed when this process is sufficiently competitive with the radiationless processes, internal conversion and intersystem crossing. The lack of fluorescence indicates that a radiationless decay dominates in solution.

The molecule being studied is 2'-acetonaphthone (2-AN) (Figure 2) a carbonyl substituted naphthalene. In general, aromatics sustituted with electron-withdrawing groups, such as the carbonyl, are non-fluorescent. In accordance with this, the 2-AN is not fluorescent in nonpolar solvents such as cyclohexane. However, a weak fluorescence has been sited in hydrogen-bonding solvents such as water.[1] This fluorescence has been speculated to occur due to the formation of a hydrogen-bonded complex between solvent and 2-AN.[2] (Figure 3)

In order to correctly interpret the spectral data to be collected, the basic properties of 2-AN absorption and fluorescence must be further understood. Absorption can occur along two axes, either parallel (^1L_b) or perpendicular (^1L_a) to the long axis of the molecule. (Figure 4) For naphthalenes such as 2-AN, the ^1L_b absorption occurs at a lower energy than the ^1L_a absorption. In general, the ^1L_a is more allowed than the ^1L_b transition. But, the longitudinal position of the carbonyl substituent dictates that the emission originates from the ^1L_b

4

FIGURE 2

Structure of 2'-Acetonaphthone
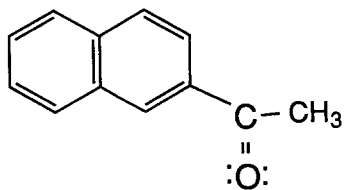
FIGURE 2

FIGURE 3

Hydrogen-Bonded Complex of

2'-Acetonaphthone

and Water

FIGURE 3
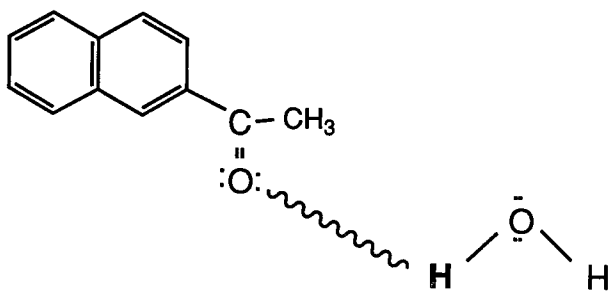
FIGURE 4

Directional Absorption Bands of

2'-Acetonaphthone

FIGURE 4
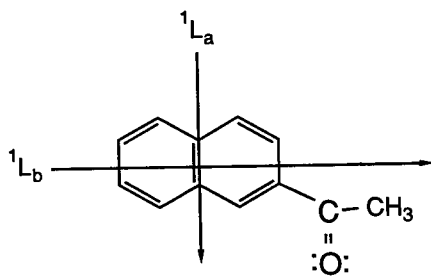
transition. Our studies are concerned primarily with the ^1L_b absorption band because the emission of the molecule occurs from this state.

Both of these directional transitions are π to π^* transitions. In the absorption study, there can also be an n to π^* transition in 2-AN which originates from the nonbonding electrons on the carbonyl. These transition types have been used to explain the 2-AN emission observed in polar solvents. (Figure 5) In nonpolar solvents, the n to π^* transition is at a lower energy than the π to π^* transition. Emission from an n to π^* state is rare, and in these solvents, radiationless decay will dominate. (Figure 6) However, when the 2-AN is solvated in polar solvents, the hydrogen bond stabilizes the nonbonding electrons which increases the energy of the n to π^* transition. Moreover, the energy of the π to π^* transition is decreased relative to the n to π^*. Since emission is more allowed from a π to π^* state, a noticeable fluorescence is seen in polar solvents. It has been speculated that this transition inversion in the polar solvents is necessary for fluorescence emission to occur.[3]

In addition to the inversion of the singlet state transitions, the hydrogen bond causes a change in the triplet state energies. The stabilization of the n-electrons by the hydrogen bond increases the energy of the $(n,\pi^*)^3$ state just as it does in the $(n,\pi^*)^1$ state. The π to π^* triplet, on the other hand, is less affected by the hydrogen bond. In nonpolar solvents the $(n,\pi^*)^1$ and the $(n,\pi^*)^3$

11

FIGURE 5

The Effect of Hydrogen Bonding

on the Transition Energies of

2'-Acetonaphthone

12

FIGURE 5

NONPOLAR
SOLVENTS

POLAR
SOLVENTS

$\Delta E_4 > \Delta E_2$

$\Delta E_3 < \Delta E_1$

13
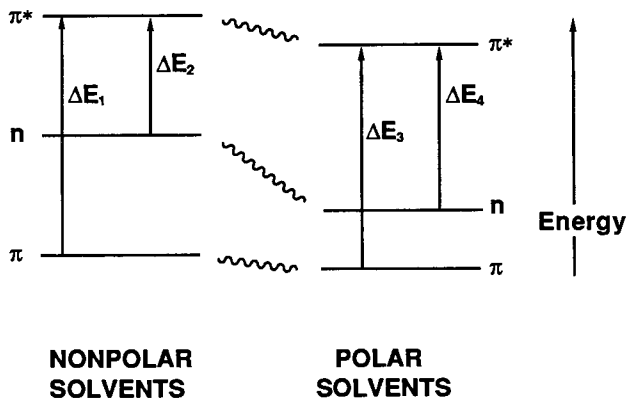
FIGURE 6

The Inversion of the

Excited State Transitions of

2'-Acetonaphthone

14

FIGURE 6

$S_2(\pi,\pi^*)$ ——— intersystem
$S_1(n,\pi^*)$ ——— crossing
⎧—$T_2(n,\pi^*)$

——$S_2(n,\pi^*)$
——$T_2(n,\pi^*)$
——$S_1(\pi,\pi^*)$

———$T_1(\pi,\pi^*)$

———$T_1(\pi,\pi^*)$

radiationless
decay

fluorescence

S_0 ———

Energy

NONPOLAR SOLVENT

POLAR SOLVENT

15
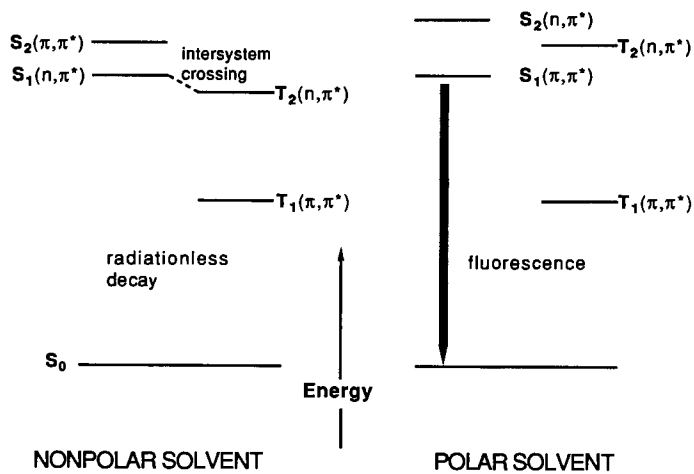
states are so close in energy that intersystem crossing dominates and no fluorescence emission is observed. (Figure 6) When the 2-AN is hydrogen bonded to water the energy difference between the $(\pi,\pi^*)^1$ and the closest lower energy triplet state, $(\pi,\pi^*)^3$, is too large for intersystem crossing to occur to a great extent. The cross from the $(\pi,\pi^*)^1$ to the $(n,\pi^*)^3$ requires thermal activation which reduces the occurrence of intersystem crossing via this pathway. Thus this reduction of the singlet to triplet transition in polar solvents allows fluorescence to occur from the $(\pi,\pi^*)^1$ state.

Our study attempts to better understand the spectral properties of 2-AN in solvents of varying hydrogen-bond donor abilities. The naphthone spectral properties have been studied in nonpolar solvents such as perfluorhexane (PFH) and cyclohexane which have no potential to hydrogen bond with the 2-AN, in methanol and ethanol, which are weak hydrogen bond donors, and in, strong hydrogen bond donors such as water, trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP). (Figure 7) By using this range of solvent hydrogen-bond donation, a correlatation may be made between the formation of the hydrogen-bonded complex and changes in both electronic absorption and fluorescence emission.

In addition, we are studying how changes in a mixed solvent environment affects the spectral properties of 2-AN. One system involves naphthone solvated in a nonpolar solvent to which are added volumes of one of the fluorinated alcohols. The other consists of the 2-AN dissolved in a polar solvent, water, where fluorescence is observed. Repeated additions of weak

16

FIGURE 7

Structures of Solvents

FIGURE 7

NON-HYDROGEN BONDING SOLVENTS

$$F-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-F$$
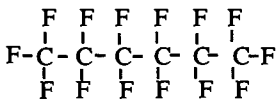
PERFLUOROHEXANE (PFH)   CYCLOHEXANE

HYDROGEN BONDING SOLVENTS

$$F-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-F \qquad\qquad F-\underset{\underset{F}{|}}{\overset{\overset{F}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH$$
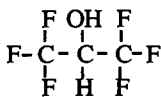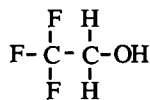
1,1,1,3,3,3-HEXAFLUORO-   2,2,2-TRIFLUOROETHANOL
      ISOPROPANOL

         (HFIP)   (TFE)

18

hydrogen-bond donors such as ethanol are made to this solution to see the effects on the emission of the 2-AN in the mixed solvent.

The Benesi-Hildebrand equation will be used to calculate equilibrium constants for the complexes being formed between the 2-AN and the hydrogen bond donor. This equation assumes a one to one complex between 2-AN (F) and the hydrogen bond donor (H).
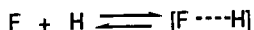
$$F \ + \ H \ \rightleftharpoons \ [F \ \text{----} \ H]$$

The equilibrium expression for the complex formation is given in equation 1.

$$K = \frac{[FH]}{[F] \, [H]} \tag{1}$$

Substituting the initial 2-AN concentration (C_F) and the initial concentration of alcohol (C_H) gives equation 2 where $(C_F\text{-}[FH])$ is the equilibrium concentration of 2-AN and $(C_H\text{-}[FH])$ is the equilibrium concentration of alcohol.

$$K = \frac{[FH]}{(C_F\text{-}[FH]) \, (C_H\text{-}[FH])} \tag{2}$$

When the initial concentration of alcohol is much greater than the concentration of the complex which is formed $(C_H \gg [FH])$ the preceeding expression is reduced to equation 3.

$$K = \frac{[FH]}{(C_F-[FH]) \, (C_H)} \qquad (3)$$

According to Beer's Law the absorbance of the complex is directly related to the concentration present in solution where A is absorbance, b is the path length and a_{FH} is the molar absorptivity of the complex at the chosen wavelength.

$$[FH] = \frac{A}{ba_{FH}} \qquad (4)$$

The absorbance equality is substituted into equation 3 to give the following equation.

$$K = \frac{\dfrac{A}{ba_{FH}}}{\left(C_F - \dfrac{A}{ba_{FH}}\right) C_H} \qquad (5)$$

Equation 5 is rearranged to solve for absorbance.

$$A = \frac{(K)(C_F)(C_H)(ba_{FH})}{[1 + (K\,(C_H))]} \qquad (6)$$

The inverse of this equality provides a straight line equation.

$$\frac{1}{A} = \left(\frac{1}{(K)(C_F)(ba_{FH})}\right) \left(\frac{1}{C_H}\right) + \left(\frac{1}{(C_F)(ba_{FH})}\right) \qquad (7)$$

Equation 8 is analogous to equation 7 but it is in terms of

fluorescence where quantum yield (ϕ_{FH}) is substituted for absorbance.

$$\frac{1}{F} = \left(\frac{1}{(K)(C_F)(\phi_{FH})}\right)\left(\frac{1}{C_H}\right) + \left(\frac{1}{(C_F)(\phi_{FH})}\right) \quad (8)$$

Therefore, according to equations 7 and 8, if 1/A or 1/F is plotted versus $1/C_H$ the slope of the straight line is equal to the equilibrium constant.

$$K = \frac{intercept}{slope} \quad (9)$$

This method of analysis has been used before to study similar systems.[2,4]

EXPERIMENTAL

Reagents: The fluorophore studied, 2'-acetonaphthone(2-AN), was purchased from Aldrich Chemical, Co and twice recrystallized in n-hexane. The melting point of the purified 2-AN is 53-4°C and the bottle sites the melting point as 53-55°C. The solvents, perfluorohexane(PFH),trifluoroethanol(TFE),hexafluoroisopropanol (HFIP), 1-butanol, 1-propanol ethanol, methanol and acetonitrile were also purchased from Aldrich Chemicals, Co. A special spectrophotometric grade cyclohexane was purchased from Mallinckrodt to reduce interferent emission from the solvent.

Instrumentation: The fluorescence measurements were obtained on a Perkin-Elmer Lambda 5B Spectrofluorometer. All spectra, both excitation and emission, were corrected for the wavelength dependence of the source, monochromator and detector and read-out on a Perkin-Elmer GP-100 Graphics Printer or a Perkin-Elmer R100A Recorder. All spectra were taken using slit widths of 10, a scan speed of 120nm/min and a response time of 3.

A Perkin-Elmer Lambda 3B UV/Vis Spectrophotometer was used to obtain absorption data. The instrument is interfaced with the Perkin-Elmer 3600 Data Station, and a Perkin-Elmer 660 Printer is used for the print-out of spectra. When not connected to the computer, the Lambda 3B output was recorded on a Perkin-Elmer R100A Recorder. All spectra were obtained at a scan speed of 120nm/min or 60nm/min.

The Infrared spectra were collected using a Perkin-Elmer 283B Infrared Spectrometer.

Procedure: The Molar Absorptivity (a) was determed for 2-AN in cyclohexane at 340nm. The absorbance of a solution of a known concentration of 2-AN in cyclohexane was measured. Using Beer's Law, A=abc, the molar absorptivity was calculated to be 1692 $l \cdot cm^{-1} \cdot mol^{-1}$ at 340nm for 2-AN in cyclohexane. This agrees with the literature value of 1650 $l \cdot cm^{-1} \cdot mol^{-1}$ at 349nm in methanol[5], providing a constant which can be used in further studies to determine concentration from 2-AN absorbance at a given wavelength.

Infrared Spectroscopy was used to confirm the presence of the hydrogen-bonded complex suggested in the literature. A 10ml solution of 2-AN in cyclohexane having a concentration is 0.01M was scanned over the region 1800-1600cm^{-1} in a 0.1mm cell. Similar solutions containing 0.01M 2-AN and 0.025M ethanol in cyclohexane and 0.01M 2-AN and 0.25M HFIP in cyclohexane were also scanned over the same region. For all the solutions the carbonyl peak occurred at 1690cm^{-1}.

The absorption and fluorescence of 2-AN were studied in pure solvents which have varying hydrogen-bond donor abilities. The solvents used were PFH, cyclohexane, ethanol, methanol, water TFE and HFIP. When taking absorption measurements, the 2-AN was dissolved in the solvent to give an absorbance ranging from 0.75 to 1.0A at 340nm so that optimum absorption data could be collected.

23

All solutions are referenced to a cell containing the pure solvent. The spectra were scanned from 315 to 370nm to include the entire π to π^* (^1L_b) absorption band.

The fluorescence of 2-AN was studied in the same solvents. All the solutions of 2-AN were prepared to have similar absorbance values (0.1) at the exciting wavelength (usually 335nm).

The pure solvent must also be scanned exciting at 335nm to insure there is no emission from the solvent. There is no emission from any of the solvents over the range which was studied. When comparing solutions with different fluorescence intensities, we used the solution with the greatest emission to set the scale of the instrument using the pre-scan mode. The emission limits were extended to a wavelength where the emission is reduced to less than 10% of its original intensity.

The quenching of 2-AN emission was studied in a mixed solvent environment. A stock solution of 2-AN was prepared in water to have an $A_{335}=0.50$. Six 10ml solutions were prepared to have the same absorbance at 335nm (0.05) by using 1ml of the stock and the appropriate volumes of water and quencher needed to provide the desired mole fractions of the latter. The range of the mole fraction of quenchers is 0 to 0.26. The quenchers used were ethanol, n-propanol, n-butanol and acetonitrile. The fluorescence intensity scale was set using the solution with no quencher added. Each sample was excited at 335nm and the emission limits were 365 to 555nm. The emission of each solution was recorded and relative intensities plotted versus mole fraction quencher.

24

Mixed-solvent studies were also performed with 2-AN dissolved in a nonpolar solvent, either PFH or cyclohexane, which has one of the fluorinated alcohols, TFE or HFIP, added to it. For the absorption studies, the 2-AN solution were all prepared to have an A_{340} of 0.5 to 1.0.

There were two methods employed for obtaining the data. The first was the single container technique. This method uses a single container of a solution of 2-AN in a nonpolar solvent (cyclohexane or PFH) which had an absorbance within the appropriate range. Sucessive additions of the fluorinated alcohols were made to this single container. Once an aliquot was made a spectrum was recorded. The cell volume is then returned to the original volume and another aliquot is added. Spectra are obtained after each of the successive additions to see the change in the spectrum of the 2-AN. The volume of added alcohol was not significant relative to that of the original solution.

When cyclohexane was used as the solvent the volume of the original solution was 50ml and the alcohol additions were over a range of 20 to 100μl. However, when PFH is the solvent, the single container studies were performed with a 6 or 3ml total volume and 1 or 2μl additions of alcohol. For the 3ml studies, alcohol additions were made directly to the cell, whereas the 6ml volume measurements were performed in a simlar fashion to the larger volume method. These small volumes of PFH were necessary to preserve the expensive solvent.

The second technique for these mixed-solvent studies is a

multi-container method. A 2-AN stock was prepared from which a series of solutions could be made in either 25 or 10ml volumetric flasks. The absorbance of the 2-AN in each of the solutions of the series is the same. Between 10 and 50μl of fluorinated alcohol were added to each of these volumetrics . The alcohol additions did not change the total volume of the solutions to any great extent. A spectrum was obtained for each of the solutions.

The range of alcohol concentration used in this experiment was obtained from literature sources reporting similar studies.[2,4] The HFIP was used over a range of 0 to 23mM, while the TFE addition included a larger range, 0 to 50mM. The ranges are the same for each of the methods used. However, the volumes vary according to the total volume of solution.

Using the same alcohol ranges, we made similar measurements on the fluorescence of these systems. The exciting wavelength was chosen from the absorption spectrum by selecting either the wavelength maxiumum 2-AN absorption or the wavelength of the isosbestic point. The emission limits were fixed so as to include the entire emission band.

Both the multi-container and the uni-container techniques were used to study the cyclohexane systems. A 50ml volume was used for the latter studies. The fluorescence intensity scale was set using a solution which had the same 2-AN absorbance at the exciting wavelength with a volume of alcohol equal to that of the final concentration to be added. All the solutions were measured with this scale.

When the multi-container method was employed, the volumes used were 10 or 25ml. All the solutions were prepared to have the same 2-AN absorbance at the exciting wavelength. The solution with the greatest alcohol concentration was used to set the intensity scale.

Only the single-container method was used for the PFH systems. The fluorinated alcohol was added in $1\mu l$ aliquots to a 3ml volume in the fluorescence cell. The scale was set with a solution whose concentration of alcohol was the same as that for the maximum volume to be added.

RESULTS

Infrared Spectroscopy was used to see the effect of hydrogen bonding on the absorption of the carbonyl substituent of the 2-AN. For all of the solutions scanned, the carbonyl absorbed at $1690 cm^{-1}$. The original 2-AN in cyclohexane solution and that with ethanol have similar sharp carbonyl absorption bands. (Figure 8) However, the solution with HFIP added to it has a broader absorption band. (Figure 9) The addition of either of these alcohols to the 2-AN solution does not change any of the surrounding absorption bands, only the carbonyl band is affected when a strong hydrogen bond donor is present in solution.

The study of 2-AN in pure solvents allows us to examine the properties of the naphthone in solvents of varying hydrogen-bond donor abilities. The π to π^* absorption band is the major concern of this study because it is the most intense absorption occurring in solution. The n to π^* absorption is hidden in the long wavelength tail of the π to π^* band.

Figure 10 shows the 2-AN absorption in some of the solvents used: HFIP, water, ethanol and PFH. The greatest red-shifted absorption is observed in HFIP, the best hydrogen-bond donor solvent. However, all the solvents have a lower energy absorption relative to that of 2-AN in PFH. Also, the 2-AN absorption band in PFH is much sharper than in the other solvents because there is virtually no interaction between solvent and 2-AN. The wavelength maximum of 2-AN absorption is the same in ethanol and methanol,

28

FIGURE 8

Infrared Absorption

of 2-AN in cyclohexane and

2-AN in cyclohexane plus ethanol

29

FIGURE 8
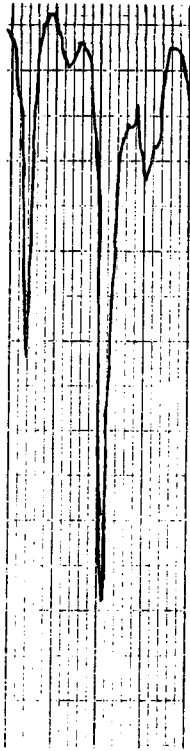

**2-AN IN
CYCLOHEXANE**

**2-AN IN
CYCLOHEXANE
PLUS ETHANOL**

30
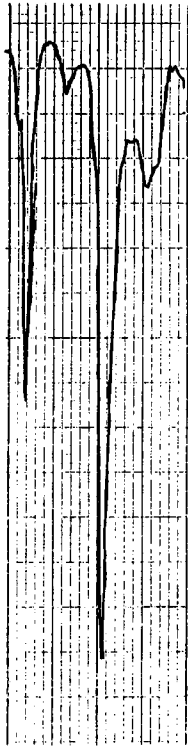
FIGURE 9

Infrared Absorption

of 2-AN in cyclohexane and

2-AN in cyclohexane plus HFIP
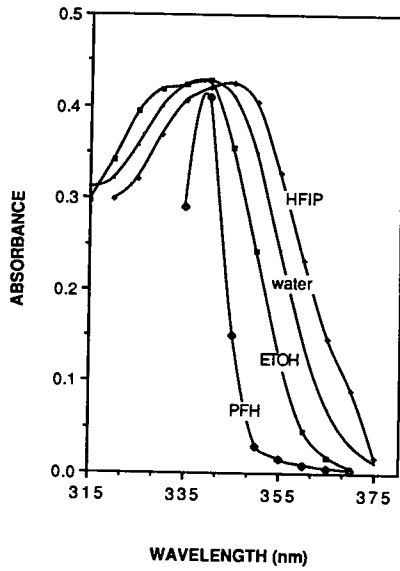
FIGURE 9

2-AN IN
CYCLOHEXANE

2-AN IN
CYCLOHEXANE
PLUS HFIP

32

FIGURE 10

Absorption Spectra of

2'-Acetonaphthone

in Solvents of Varying

Hydrogen-Bond Donor Abilities

FIGURE 10

34

and the 2-AN in TFE has a similar absorption spectra to that in water.

In Table 1 there is a listing of the maximum absorption wavelength of 2-AN in the different solvents used. The α value in this table is a constant which reflects the hydrogen-bond donor ability of a particular solvent. A value for HFIP could not be found; however, since it is known to be a better hydrogen-bond donor than TFE,[4] we are confident in assuming that α for HFIP is greater than that of TFE. Clearly, the π to π^* absorption red shifts as hydrogen-bond donation from the solvent increases.

The literature suggests that there is no fluorescence emission of 2-AN is nonpolar solvents such as PFH and cyclohexane. Our data confirm this because even at high 2-AN absorbances there is no emission observed in these solvents. In addition, no emission was seen in the weak hydrogen-bonding solvents, ethanol and methanol. However, there is an emission noted in water, TFE and HFIP. (Figure 11)

The fluorescence quantum yield (ϕ_f) was determined for 2-AN in each of the solvents by comparison to quinine sulfate in 1.0N sulfuric acid as the standard. The quantum yield is a constant which relates the number of photons emitted relative to the amount of photons absorbed.

$$\phi_f = \frac{\text{photons emitted}}{\text{photons absorbed}} \qquad (10)$$

TABLE 1

Summary of Hydrogen Bonding

Effects on the Spectral Properties of

2'-Acetonaphthone in Pure Solvents

TABLE 1

solvent	$\alpha^{(1)}$	λ_{abs} (nm)	λ_{fluor}(nm)	$\phi_f^{(2)}$
Ethanol	0.85	335	---	0
Methanol	0.98	335	---	0
Water	1.10	$338^{(3)}$	$434^{(3)}$	0.061
TFE	1.61	339	431	0.091
HFIP	>1.61	345	451	0.33

[1] Kamlet-Abboud-Taft parameter which measures hydrogen-bond donor strength of a solvent

[2] ϕ_f = fluorescence quantum yield :

$$\frac{\text{photons out(fluorescence)}}{\text{photons in(absorbance)}}$$

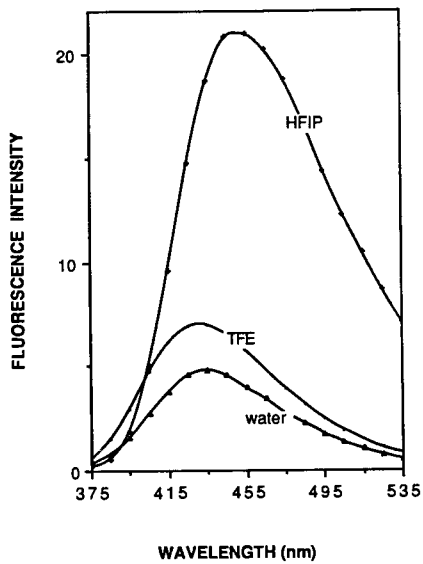[3] literature lists λ_{abs}=343nm and λ_{fluor}=438nm from

Kovi, P.J, A.C. Capomacchia, and S.G. Schulman *Spectroscopy Letters*, **1973**, 6, 7-22.

FIGURE 11

Fluorescence Spectra of

2'-Acetonaphthone

in Hydrogen Bonding Solvents

FIGURE 11

The ϕ_f of this standard is 0.546.[6] Solutions of 2-AN in water and quinine sulfate in 1.0N sulfuric acid were prepared having equal absorbances which were <0.05 at the exciting wavelength (335nm). The ϕ_f of 2-AN in water was then calculated according to the following equation, where F(2-AN) and F(QS) are the areas under the corrected fluorescence emission spectra of these solutions.

$$\phi_f(2\text{-AN}) = \frac{F(2\text{-AN}) \ x0.546}{F(QS)} \qquad (11)$$

The ϕ_f values for 2-AN in HFIP and TFE were estimated by comparing their relative fluorescence intensities with that of 2-AN in water for equal absorbances at the exciting wavlength.

As listed in Table 1, the greatest quantum yield for 2-AN is found in HFIP. The ϕ_f of 2-AN in TFE is greater than that of 2-AN in water. Since no emission is observed in ethanol or methanol the ϕ_f is zero. Also, the emission of 2-AN in HFIP is red-shifted relative to that in TFE or water. Thus, the solvent with the greatest hydrogen-bond donor ability has the lowest energy emission and greatest ϕ_f. However, the emission of 2-AN in water occurrs at a lower energy than the TFE, which is the reverse of the relative quantum yields.

Not only does 2-AN not fluoresce in pure ethanol, but ethanol quenches the fluorescence emission of 2-AN in water. Even mole fractions of ethanol as a small as 0.016 cause a notable reduction in the emission. (Figure 12 and Table 2) Studies similar to these

40

FIGURE 12

Fluorescence Emission Spectra of

2'-Acetonaphthone

in Water Quenched by Ethanol

41

FIGURE 12

Y-axis: FLUORESCENCE INTENSITY (20, 10, 0)

X-axis: WAVELENGTH (nm) — 365, 405, 445, 485, 525

Legend: mole fraction ethanol
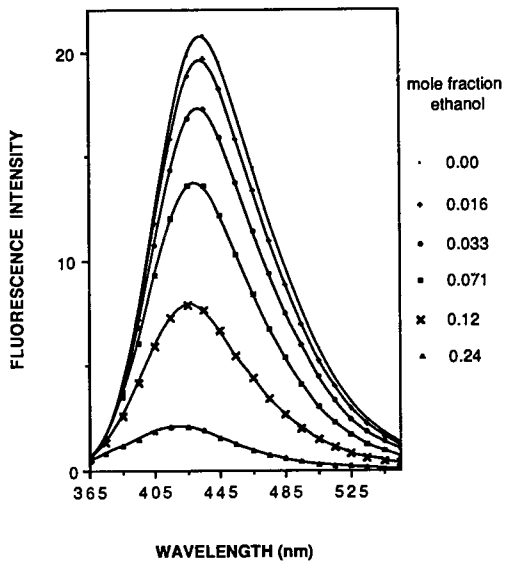- 0.00
- 0.016
- 0.033
- 0.071
- 0.12
- 0.24

42

TABLE 2

Quenching by Ethanol

TABLE 3

Quenching by Acetonitrile

TABLE 4

Quenching by Propanol

TABLE 2

mole fraction ethanol	λmax(nm)	Relative Intensity
0.0	433	1.0
0.016	432	0.94
0.033	431	0.83
0.071	430	0.66
0.12	428	0.38
0.24	420	0.10

TABLE 3

mole fraction acetonitrile	λmax(nm)	Relative Intensity
0	434	1.0
0.0070	433	0.91
0.013	433	0.84
0.021	432	0.74
0.029	431	0.66
0.037	430	0.57
0.13	424	0.12
0.26	420	0.025

TABLE 4

mole fraction propanol	λmax(nm)	Relative Intensity
0.0	432	1.0
0.016	431	0.89
0.035	430	0.79
0.057	428	0.45
0.074	427	0.27
0.11	421	0.12
0.23	417	0.054

44

were also performed with n-propanol, n-butanol and acetonitrile. (Figure 13 and Table 3 and Figure 14 and Table 4) The n-butanol was too nonpolar to be miscible in large mole fractions.

The effects appear to be qualitatively the same with all of the quenchers. The emission decreases with increased mole fraction of quencher and the emission maximum also blue shifts. All of the quenchers were studied over similar ranges, 0-26 mole percent quencher. The amount of quenching seems relatively constant for the three studied. The acetonitrile is the best quencher, reducing the emission to less than one percent of the original intensity. (Figure 15 and Table 5) The propanol also quenches the intensity to less than a percent of the original value. The ethanol, however, is the least efficient of the three over the range used; the final intensity is decreased to ten percent of the emission seen with no quencher present. The solution which is 0.016 mole fraction butanol had a five percent reduction in intensity. This is equal to the decrease seen with the propanol and acetonitrile but greater than the quenching of ethanol at this mole percent.

Also, the degree of blue shift does not vary among the quenchers. There is a 13-15nm shift of the maximum over the ranges used. (Table 5) The blue shift (438 to 434nm) which is seen with butanol addition is much larger than the shift seen with the other quenchers at this same mole fraction (0.016).

Other mixed solvent studies also show how the solution environment affects the spectral properties of 2-AN. The 2-AN has

45

FIGURE 13

Fluorescence Emission Spectra of
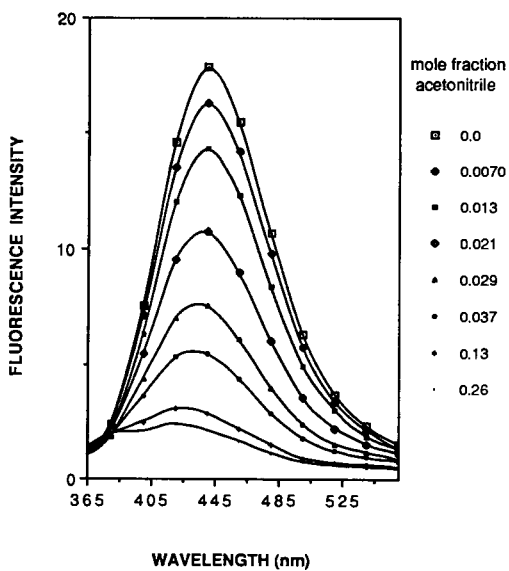
2'-Acetonaphthone

in Water Quenched by Acetonitrile

46

FIGURE 13

WAVELENGTH (nm)

47

FIGURE 14

Fluorescence Emission Spectra of

2'-Acetonaphthone

in Water Quenched by Propanol

FIGURE 14

Graph of FLUORESCENCE INTENSITY versus WAVELENGTH (nm), with curves for different mole fraction propanol values:

mole fraction propanol
0.0
0.016
0.035
0.057
0.074
0.11
0.23

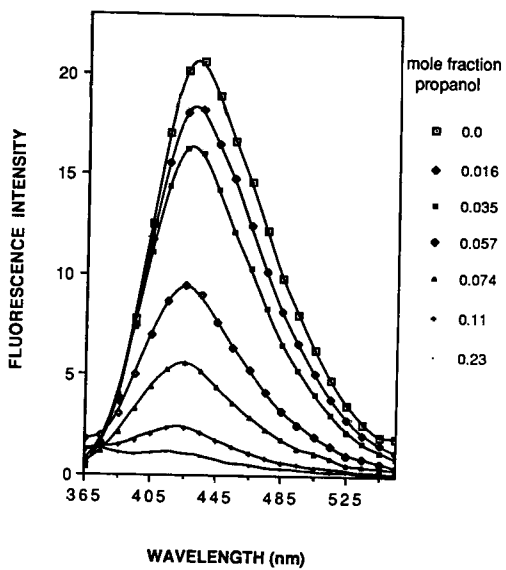**FIGURE 15**

Summary of Quenching Data

Relative Fluorescence Intensity

vs. Mole Fraction Quencher

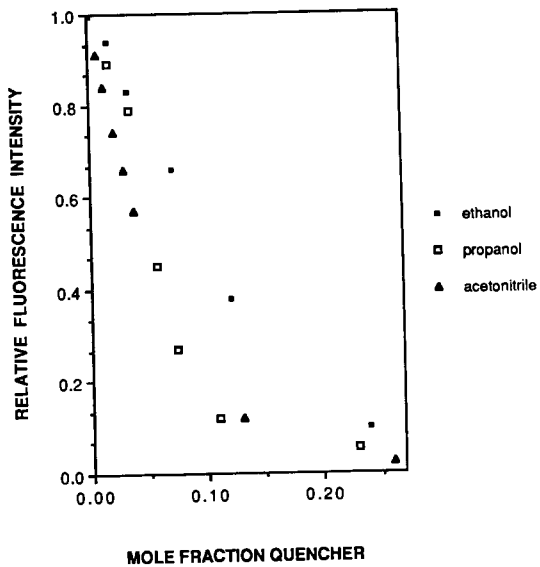**FIGURE 15**

MOLE FRACTION QUENCHER

51

TABLE 5

Summary of Quenching Results

TABLE 6

Equilibrium Constants for

Complex Formation of

2'-Acetonaphthone in Cyclohexane

Plus TFE or HFIP

TABLE 5

Quencher	range of quencher (mole fraction)	$\Delta\lambda$ (nm)	final relative intensity
ethanol	0-0.24	13	0.10
propanol	0-0.23	15	0.054
acetonitrile	0-0.26	14	0.025
butanol	0-0.016	4	0.85

TABLE 6

Solvent	Alcohol	Equilibrium Constant
cyclohexane	TFE	31+/-9
cyclohexane	HFIP	91+/-5

53

a single absorption peak when dissolved in the nonpolar solvent, but as a fluorinated alcohol is added there is a increasing absorption at longer wavelength. This secondary absorption is seen with all of the systems studied. (Figures 16A, 17A, 18, and 19) Only the two systems where cyclohexane is the solvent have an isosbestic point at 325nm. (Figures 16A and 17A) The PFH systems do not possess this common point but rather show an overall increase in absorption across the whole spectrum.

Using the Benesi-Hildebrand equation, equilibrium constants were calculated for some of these systems. (Figures 16B and 17B and Table 6) There was a great deal of variation in the equilibrium values calculated for the systems in PFH. The Benesi-Hildebrand plots were not linear which indicates that this method could not be used to determine the equilibrium values for these systems.

In addition, fluorescence was studied for these nonpolar-fluorinated alcohol systems. There is no fluorescence seen when TFE was added to the 2-AN in cyclohexane. Therefore, no Benesi-Hildebrand equilibrium constants could be calculated. Due to the lack of fluorescence emission in the cyclohexane system the system with 2-AN in PFH plus TFE was not tested.

However, when HFIP is added to a nonfluorescent 2-AN in PFH or cyclohexane solution an emission is observed. There is variation in the spectra obtained from this system. The emission of a given solution changes with respect to time or agitation. These inconsistencies observed prohibited any further investigation of

54

FIGURE 16A

Absorption Spectra of 2-AN in
Cyclohexane plus TFE

FIGURE 16B

Benesi-Hildebrand Plot of
Absorption Data from
2-AN in Cyclohexane plus TFE
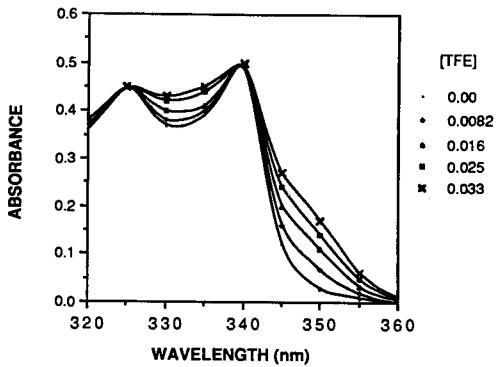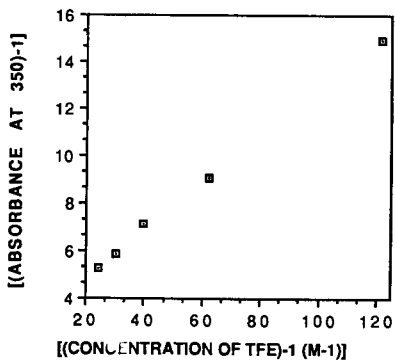
55

FIGURE 16A

FIGURE 16B

FIGURE 17A

Absorption Spectra of 2-AN in

Cyclohexane plus HFIP

FIGURE 17B

Benesi-Hildebrand Plot of

Absorption Data from

2-AN in Cyclohexane plus HFIP

FIGURE 17A
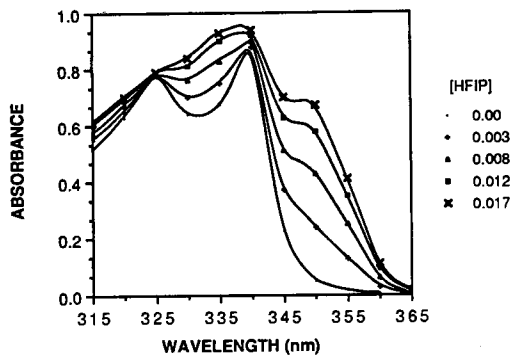
FIGURE 17B
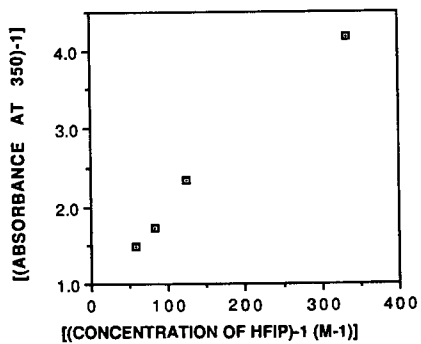
58

FIGURE 18

Absorption Spectra of

2'-Acetonaphthone

in PFH Plus TFE

59
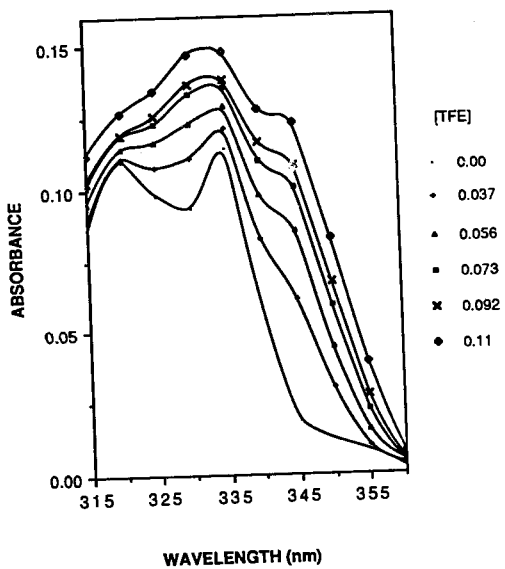
FIGURE 18

FIGURE 19

Absorption Spectra of

2'-Acetonaphthone

in PFH Plus HFIP

61

FIGURE 19

Figure 19. Plot of ABSORBANCE vs WAVELENGTH (nm) for [HFIP] concentrations: 0.00, 0.0025, 0.0050, 0.0075, 0.010, 0.013.

62
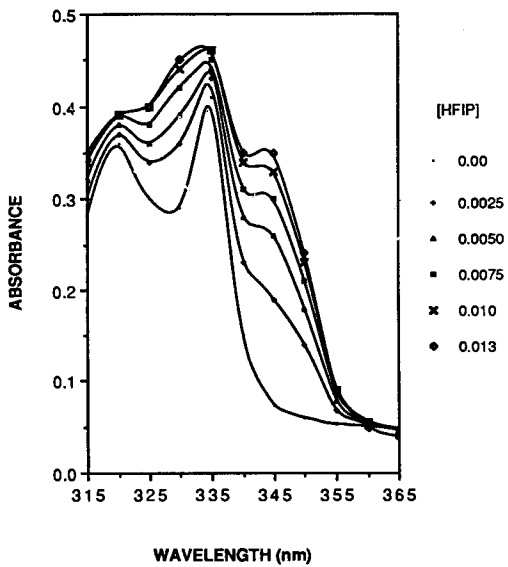
this system. Moreover, the 2-AN in PFH which had HFIP additions shows an increasing fluorescence with increasing concentration of fluorinated alcohol. This emission is, however, accompained by a red shift in the wavelength of maximum emission. (Figure 20) The Benesi-Hildebrand equation could not be used for these fluorescence investigations because of the variation among the spectra of a given system.

FIGURE 20

Fluorescence Spectra of

2'-Acetonaphthone

in PFH Plus HFIP

64

FIGURE 20

FLUORESCENCE INTENSITY

[HFIP]

▲ 0.0125M

✕ 0.0100M

● 0.0075M

● 0.0050M

◆ 0.0025M

· 0.00M

WAVELENGTH(nm)

65
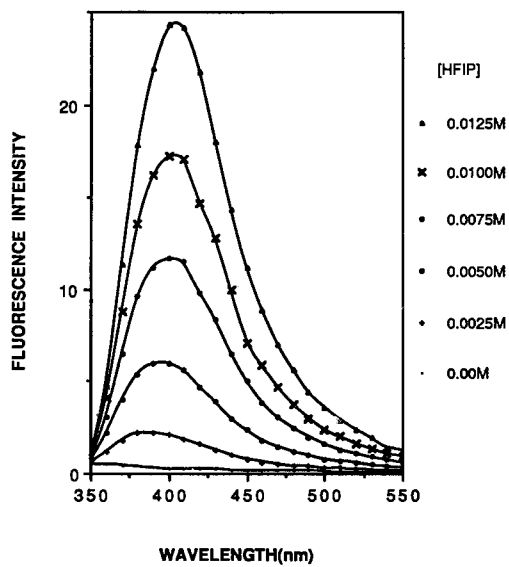
DISCUSSION

The broadening of the carbonyl IR absorption band proves that there is hydrogen bonding present in the solution of 2-AN in cyclohexane plus HFIP. Since there is no change in the band when ethanol is present in solution, the ethanol is not a strong enough hydrogen bond donor to form a significant complex with 2-AN. Despite the larger α value of methanol, both methanol and ethanol appear to have the similar electronic absorption spectra, indicating there is no significant difference in hydrogen bonding to 2-AN in these two solvents. (Table1) Similarly, the lack of fluorescence emission further indicates the insignificance of the hydrogen bonding between 2-AN and these two solvents. However, previous investigations suggest evidence for ethanol hydrogen bonding to 2-AN at 77°K.[3] These studies report a complex absorption upon the addition of ethanol to a nonpolar mixture of isopentane and methyl cyclohexane. Also, when small additions (0.05%) of ethanol are made to the nonpolar solution, an emission band is observed at 350nm. This study suggests that hydrogen bonding at 77°K is significant enough to form the complex with 2-AN resulting in changes in the absorption and the fluorescence spectra of the 2-AN. Our results indicate that such hydrogen bonding interactions are not strong relative to available thermal energies at room temperature.

The studies in pure solvents further illuminates the effect that hydrogen bonding has on the spectral properties of 2-AN.

Table 1 shows a direct correlation between the hydrogen bond donor ability of a solvent (α) and energy of the π to π^* absorption. In HFIP, which is the strongest hydrogen bond donor solvent, 2-AN has the lowest absorption energy and fluorescence emission energy and the greatest quantum yield (0.33). This is similar to that of anthracene (0.36)[7], a known moderate fluorescer.

The quantum yield of 2-AN in TFE is greater than that in water. However, the absorption energies of 2-AN in these two solvents are nearly equal. Also, in water 2-AN has a lower emission energy than in TFE. The higher ϕ_f value for 2-AN in the TFE indicates that this solvent is more effective than water at blue-shifting the (n,π^*) energy. It also suggests that the shift of the (n,π^*) is more important than the red shift of the (π,π^*) transition for the excited state inversion which is necessary for fluorescence emission in these hydrogen bond donor solvents.

The pure solvent studies suggest that the weaker hydrogen bonding alcohols such as ethanol and methanol are not strong enough hydrogen bond donors to complex significantly with the 2-AN at room temperature. But solvents such as these have been found to be efficient quenchers of fluorescence emission in water. The addition of the quenchers also blue shifts the emission maximum of 2-AN. (Figures 12, 13, and 14) The combination of blue shift and decrease in emission as the concentration of quencher increases suggests that the quencher is preferentially dissolving the 2-AN in less polar "pockets" in the interstices of the water lattice. The 2-AN hydrogen bonds to the water at the

surface of these pockets, thereby still enabling fluorescence to result. However, as the concentration of quencher increases, the 2-AN is less able to hydrogen bond with the water and the fluorescence emission decreases. Also, as these pockets get larger the environment of the 2-AN is more hydrophobic which accounts for the blue shift of the maximum as the concentration of quencher increases.

This effect is seen with all of the quenchers used. Acetonitrile is the most efficient fluorescence quencher over the range of added quencher. On the other hand, butanol possesses the largest nonpolar hydrocarbon chain which increases the hydrophobic character of the solution more than the smaller chained alcohols or the acetonitrile which would account for the large blue shift observed with this quencher at small mole fractions. (Table 5)

The additional mixed solvent systems involving cyclohexane or PFH as the main solvent illustrate some of the other effects of solvent environment on the spectral properties of 2-AN. The absorption at longer wavelengths which results when TFE or HFIP is added is due to the 2-AN/alcohol complex. (Figures 16A, 17A, 18, and 19) As the concentration of hydrogen-bond donor increases the concentration of the complex increases. In cyclohexane, a larger equilibrium constant is seen when the fluorinated alcohol is HFIP than TFE because HFIP is known to be a better hydrogen bond donor than TFE.[4] (Table 6)

The lack of reliable results in the PFH systems is probably

68

consistent with the absence of an isosbestic point in the spectra of 2-AN upon addition of TFE or HFIP. (Figures 18 and 19) The presence of this point in the cyclohexane systems indicates that a simple 1:1 equilibrium is probably occurring upon alcohol addition. (Figures 16A and 17A) The lack of an isosbestic point in PFH plus HFIP may be due to the changing solvation of the 2-AN in the HFIP. (Equation 12)

$$2\text{-AN}_{(PFH)} + HFIP \rightleftharpoons 2\text{-AN--HFIP}_{(PFH)} \rightleftharpoons 2\text{-AN--HFIP}_{(HFIP)} \qquad (12)$$

The 2-AN is not as soluble in PFH as it is in HFIP; therefore, when the alcohol is added, the 2-AN/HFIP complex may prefer to be dissolved by the alcohol and the equilibrium of the system may lie on the right of equation 12. If the spectra of the complex differs in these two environments, no isosbestic point would be seen.

For various reasons the fluorescence data of 2-AN in these mixed solvent systems are too unreliable to yield any complex equilibrium constants. The TFE is apparently not a strong enough hydrogen bonder to complex the 2-AN in cyclohexane because no fluorescence is seen which it is added to 2-AN in this solvent. Also, the emission intensity of 2-AN in cyclohexane plus HFIP vaires with time which disallows the application of the Benesi-Hildebrand equation. The red shifting of the emission maximum upon the addition of HFIP to 2-AN in PFH may be due to the preferred solvation of 2-AN by the HFIP. (Figure 20 and Equation 12) The emitting species in the solution may be changing or the quantum yield could be varying, both of these could account

69

for the spectral variance seen with this system. In any case, the Benesi-Hildebrand equation can not be used in this case either.

When the relative change in the complex absorbance and fluorescence are plotted versus the concentration of HFIP added to 2-AN in PFH, the data suggest that there is stronger complex formation in the excited state. (Figure 21) The absorbance appears to plateau at the higher concentrations of HFIP. The fluorescence, on the other hand, continually increases as the HFIP concentration increases. This indicates a stronger interaction of the 2-AN and the HFIP in the excited state. In the excited state there is an increased charge-transfer onto the carbonyl which will enhance its ability to hydrogen bond. (Figure 22) This increased affinity for the fluorinated alcohol in the excited state may account for the increased solubility of the 2-AN complex in HFIP. This may also be a reason that the system does not conform to the Benesi-Hildebrand equation, since the quantum yield of the complex may not be constant with increasing HFIP concentration.

FIGURE 21

2'-Acetonaphthone

in PFH Plus HFIP:
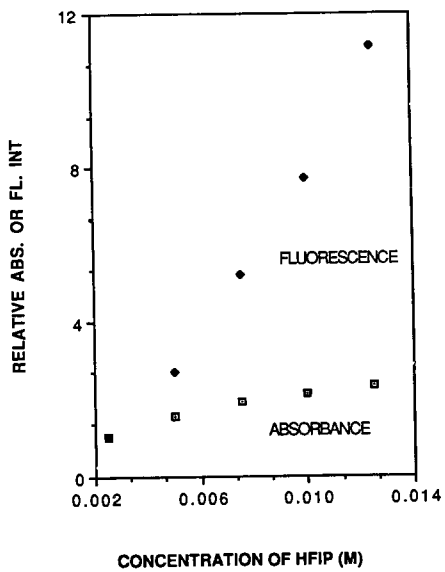
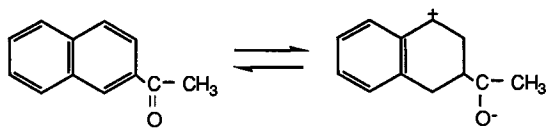Hydrogen Bonding in

the Excited State

FIGURE 21

CONCENTRATION OF HFIP (M)

FIGURE 22

Excited-State Resonance of

2'-Acetonaphthone

FIGURE 22

FUTURE WORK

The problems encountered in the mixed solvent systems limits the investigation in that area. However, the quenching experiments can be continued to attempt to further the understanding of the workings of the system. The quenchers to be tried are cyclodextrins. These molecules have a "cage" in which the 2-AN molecule can fit.

Also, further attempts to characterize the fluorescence emission include seeing how salts affect the solution's emission of 2-AN in water. Sodium perchlorate ($NaClO_4$) is a structure breaker and magnesium sulfate ($MgSO_4$) is a structure enhancer. The addition of these salts to solutions of 2-AN in water may cause changes which would further our understanding about the fluorescence of 2-AN.

REFERENCES

(1) Kovi, P.J., A.C. Capomacchia and S.G. Schulman *Spectrosc. Lett.* **1973**, 6, 7-22.

(2) Das, P.K. and G.L. Hug *Photochem. Photobiol.* **1982**, 36, 455-461.

(3) Kitamira, Michio and Hiroaki Baba *Bull. Chem. Soc. Jap.* **1975**, 48, 1191-1195.

(4) Das, P.K. and G.L. Hug *J. Phys. Chem.* **1983**, 87, 49-54.

(5) UV Atlas of Organic Compounds IV **1968**, Plenum Press, New York.

(6) Demas, J.N. and G.A. Crosby *J. Phys. Chem.* **1971**, 75, 991.

(7) Berlman, Isadore B Handbook of Fluorescence Spectra of Aromatic Molecules **1971** Academic Press, New York, 356.