conjugation of the nitrogen unshared pair of l electrons as a function of molecular geometry is taken up. Recent work in Kasha's group[23] has suggested that the angle of twist of the amine group in aromatic amines is an important factor in spin–orbit coupling in aromatic amines. The work of Godfrey and Murrell[10–12] has indicated the oscillator strength and energy dependencies on the angle of twist in aniline and some of its derivatives. Since the molecules in this study have nitrogen substituents of widely varying geometries, one can expect anomalous behavior in one compound or another. Individually, these three effects are impossible to assess for any given molecule since the geometries of these molecules still remain to be determined. There has been, however, a recent report on an X-ray crystallographic study of N-(p-tolyl)-2-aminonaphthalene-6-sulfonate.[33] Apparently the nitrogen atom in this molecule has nearly an sp^2 configuration in the ground state and thus the l electrons would interact strongly with the π-electron system of the naphthalene ring. The results presented here and in the following paper support that fact.

Conclusions

There are several important conclusions that can be

drawn from the luminescence and absorption data presented above. (1) The shapes and energies of the absorption and luminescence spectra suggest that the amounts of intramolecular charge-transfer character in the three lowest electronic states are in the order $CT(S_1)$ > $CT(T_1)$ ≥ $CT(S_0)$. (2) Protonation of the partially bonding l electrons of the nitrogen atom of all these molecules resulted in the appearance of naphthalene-2-sulfonate-like absorption and fluorescence spectra. Thus the inductive effect of the positively charged ammonium group on both the ground and first excited singlet states of the parent hydrocarbon was small. (3) The l electrons of the nitrogen atom are principly involved in the low-energy transitions in the singlet manifolds of these molecules. (4) There is a significant amount of intramolecular charge transfer in at least the two lowest energy absorptions of all these molecules. (5) The amount of intramolecular charge-transfer character in the two lowest energy absorption bands can be increased by decreasing the ionization potential of the amine group and/or increasing the electron affinity of the naphthalene ring by the addition of the sulfonate group.

(33) A. Camerman and L. H. Jensen, *J. Amer. Chem. Soc.*, **92**, 4200 (1970).

Electronic Spectra of 2-Aminonaphthalene-6-sulfonate and Related Molecules.[1] II. Effects of Solvent Medium on the Absorption and Fluorescence Spectra

Carl J. Seliskar[2] and Ludwig Brand*

Contribution from the McCollum–Pratt Institute, The Johns Hopkins University, Baltimore, Maryland 21218. Received August 26, 1970

Abstract: The solvent dependence of the absorption and fluorescence of 2-aminonaphthalene-6-sulfonate and its derivatives was measured in liquid solvents and was found to conform with a simple solvent–solute interaction scheme. Solvent relaxation is shown to be a key factor in the fluorescence, and the variations of the fluorescence quantum yields are interpreted on the basis of solvent-relaxation-facilitated intersystem crossing to the triplet state.

In the first paper in this series[3] the general characteristics of the electronic spectra of 2-aminonaphthalene-6-sulfonate and several of its derivatives were reported. In this communication the solvent dependence of the absorption and fluorescence spectra of those molecules are examined in detail.

Some of the molecules in this study, specifically the N-arylaminonaphthalenesulfonates, adsorb to specific, functionally important regions on several proteins.[4]

The fluorescence quantum yields of these compounds are low in polar liquids. When they are dissolved in nonpolar liquids or adsorbed to proteins or other macromolecules their quantum yields and energies of fluorescence increase. Since the fluorescence spectra of these adsorbed dyes closely reflect those in nonpolar liquids, they have come into wide usage as probes for hydrophobic regions on biopolymers.

It was the purpose of this research first to quantitate the solvent dependence of the luminescence and second to provide a rationale for the spectroscopic behavior of 2-aminonaphthalene-6-sulfonate and related molecules dissolved in solvents of varying static dielectric constant.

Experimental Section

In addition to those described in the previous paper, the following solvents were obtained as Spectroquality grade from Matheson
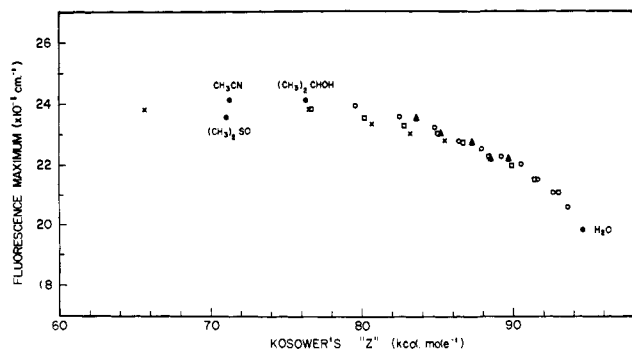
(3) C. J. Seliskar and L. Brand, *J. Amer. Chem. Soc.*, **93**, 5405 (1971).
(4) G. M. Edelman and W. O. McClure, *Accounts Chem. Res.*, **1**, 65 (1968).

Figure 1. Fluorescence maxima of N-phenyl-2-aminonaphthalene-6-sulfonate as a function of Kosower's Z. The solvents are indicated as follows: ×, acetone–water mixtures; □, dioxane–water mixtures; O, ethanol–water mixtures; ▲, methanol–water mixtures.

Figure 2. Fluorescence maxima of N-phenyl-N-methyl-2-amino-naphthalene-6-sulfonate as a function of Kosower's Z. The solvents are indicated as follows: ×, acetone–water mixtures; □, dioxane–water mixtures; O, ethanol–water mixtures; ▲, methanol–water mixtures.

Coleman and Bell: dimethyl sulfoxide, p-dioxane, acetone, 2-propanol, acetonitrile, glycerol, and methanol. The molecules, experimental procedures, and apparatus have been described previously.[3]

Results and Discussion

It is known that the fluorescence energies, bandwidths, and quantum yields of the N-arylaminonaphthalenesulfonates show a marked dependence on the dielectric constants of the solvent medium at 300°K.[5,6] It has been reported[3,6] that the fluorescence energies, bandwidths, and quantum yields correlate well with the empirical solvent scale proposed by Kosower.[7] The behavior of the fluorescence energies for N-phenyl-2-aminonaphthalene-6-sulfonate and N-phenyl-N-methyl-2-aminonaphthalene-6-sulfonate in various pure solvents and solvent mixtures is shown in Figures 1 and 2. These two molecules were studied because one has an ionizable amine proton and the other does not. Since both molecules show similar behavior as a function of Kosower's[7] Z value, it may be concluded that an amine proton is not necessary for the sensitivity of the fluorescence parameters to solvent polarity. The changes in the fluorescence spectra of these two molecules are clear. As the value of Z was increased, that is, as the dielectric constant was also increased, the energy of the fluorescence decreased. This relationship held true for all the liquid solvents that have been used. Thus the dependence of the energy on the "polarity" of the solvent at 300°K was not dependent on the specific chemical groupings of the different solvent molecules, but dependent on the solvent dielectric constant.

It has been shown that the bandwidths and quantum yields behave in a similar way.[3,6] However, the quantum yields of fluorescence are subject to specific quenching effects. These specific quenching effects are not considered here, rather only those cases where the quantum yields do follow a solvent "polarity" relationship.

For the sake of comparison of the spectroscopic properties of these molecules, the solvents ethanol and water and their mixtures were selected. There were two practical reasons for this choice. First, nearly all of the molecules were soluble in them and, second, the aryl-substituted molecules showed large changes in their
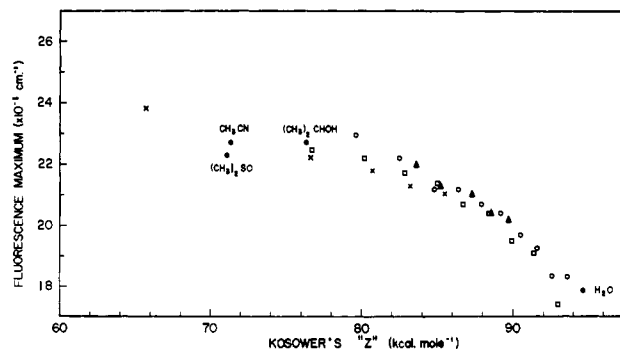
fluorescence energies, bandwidths, and quantum yields between ethanol and water.

The absorption and fluorescence data for these molecules in ethanol and water are summarized in Table I. The molecules have been arranged so that, in general, as one procedes down the list of molecules the ionization potential of the amine group decreases and/or the electron affinity of the naphthalene ring system increases. In any one solvent such as ethanol, the absorption maximum of the lowest energy transition, $\bar{\nu}_a$, decreases, in general, as one goes down the list of molecules. The values for $\bar{\nu}_a$ in ethanol are those obtained from resolving the absorption spectra into several symmetrical bands, while those in water were estimated without such curve analysis. The variation in the absorption maxima, $\bar{\nu}_a$, in any one solvent from the molecules at the beginning of the table to those at the end is about 1000 cm^{-1}. The energies of the fluorescence maxima, $\bar{\nu}_f$, in any one solvent, decrease as one proceeds down the list of molecules. Here the variation over the entire table is about 2000 cm^{-1} in ethanol and 5000 cm^{-1} in water.

A comparison of the energies of the lowest energy absorption bands, $\bar{\nu}_a$, for any single molecule in ethanol and water shows that there is a small increase in the energy in going from ethanol to water. The variation is of the order of 3000 cm^{-1}. On the other hand, the energies of the fluorescence maximum, $\bar{\nu}_f$, decrease for any given molecule in going from ethanol to water.

In ethanol, the bandwidths at half-maximum emission, $\Delta\bar{\nu}_f$, remain fairly constant, whereas in water they increase, in general, in going down the table of molecules. The two compounds N-(o-tolyl)-2-aminonaphthalene-6-sulfonate and N-(p-tolyl)-2-aminonapthalene-6-sulfonate have nearly zero fluorescence quantum yields and, thus, the measurements of their $\Delta\bar{\nu}_f$ values were difficult.

The fluorescence quantum yields in ethanol remain high (~0.5) for all the molecules except N-(p-hydroxyphenyl)-2-aminonaphthalene. This exception is in accord with what would be expected from a decrease in the ionization potential of the amine group of N-phenyl-2-aminonaphthalene.

In contrast to the results obtained in ethanol, the fluorescence energies, bandwidths, and quantum yields in water show large changes in going down the table. For any one molecule, the effect of the more polar solvent water is to decrease the energy and to increase in

(5) W. O. McClure and G. M. Edelman, Biochemistry, 5, 1908 (1966).
(6) D. C. Turner and L. Brand, ibid., 7, 3381 (1968).
(7) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968.

Table I. Absorption and Fluorescence Parameters in Ethanol and Water

Molecule	Solvent	$\bar{\nu}_a$, cm⁻¹ ± 200	$\bar{\nu}_f$, cm⁻¹	$\Delta\bar{\nu}_f$, cm⁻¹	$\bar{\nu}_a - \bar{\nu}_f$, cm⁻¹	Ω_u
2-Aminonaphthalene	Ethanol	29,200	24,710	3240	4,500	0.59
	Water	29,800	24,160	3420	5,600	0.53
2-Aminonaphthalene-6-	Ethanol	29,100	24,550	3110	4,500	0.53
sulfonate	Water	29,400	23,620	3530	5,800	0.55
N,N-Dimethyl-2-amino-	Ethanol	28,200	24,100	3180	4,100	0.54
naphthalene-6-sulfonate	Water	28,600	22,420	3320	6,200	0.77
N-Phenyl-2-amino-	Ethanol	28,800	24,350	3420	4,400	0.44
naphthalene	Water					
N-Cyclohexyl-2-amino-	Ethanol	28,200	24,080	3280	4,100	0.46
naphthalene-6-sulfonate	Water	28,600	22,750	3570	5,800	
Di-2-naphthylamine	Ethanol	28,500	23,910	3880	4,600	0.34
	Water					
N-(p-Hydroxyphenyl)-2-	Ethanol	28,000	20,100 ± 100	5600 ± 100	7,900	0.01 ± 0.005
aminonaphthalene	Water					
N-Phenyl-2-amino-	Ethanol	28,600	23,980	3460	4,600	0.65
naphthalene-6-sulfonate	Water	28,700	19,900 ± 500	5400 ± 1000	8,800	0.090 ± 0.005
N-Phenyl-N-methyl-2-amino-	Ethanol	28,300	23,080	4150	5,200	0.50
naphthalene-6-sulfonate	Water	28,400	18,400 ± 500	4600 ± 1000	10,000	0.006 ± 0.001
N-(o-Tolyl)-2-amino-	Ethanol	28,600	24,050	3640	4,600	0.57
naphthalene-6-sulfonate	Water	28,700	19,200 ± 500	4900 ± 1000	9,500	0.001 ± 0.001
N-(m-Tolyl)-2-amino-	Ethanol	28,400	23,730	3660	4,700	0.69
naphthalene-6-sulfonate	Water	28,600	19,200 ± 500	6000 ± 1000	9,400	0.003 ± 0.001
N-(p-Tolyl)-2-aminonaphtha-	Ethanol	28,000	23,090	4050	4,900	0.67
lene-6-sulfonate	Water	28,200	19,400 ± 500	4100 ± 1000	8,800	0.001 ± 0.001

bandwidth of fluorescence. Whereas the quantum yields remain generally high in ethanol, those in water decrease markedly as one proceeds down the table.
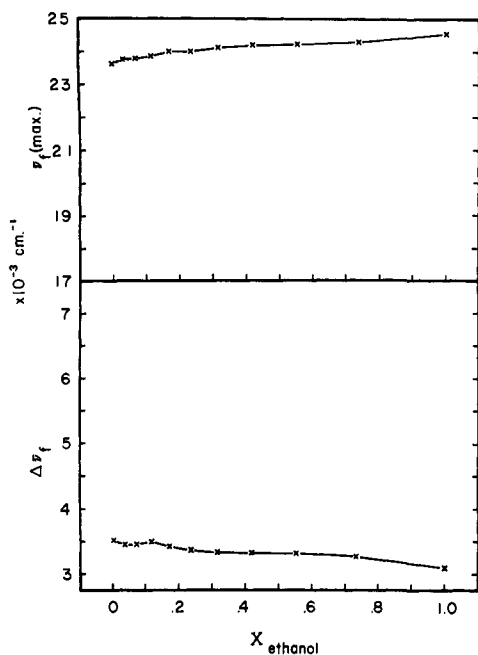

Figure 3. Fluorescence maxima and bandwidths of 2-amino-naphthalene-6-sulfonate as a function of the mole fraction of ethanol in ethanol–water mixtures.

Because of the relative changes in the values of $\bar{\nu}_a$ and $\bar{\nu}_f$, the Stokes shift, $\bar{\nu}_a - \bar{\nu}_f$, remains roughly constant in ethanol but increases in water in going down the list of molecules.

From the data in Table I the following inferences may be made. (1) The magnitude of the fluorescence changes in any one molecule in going from an ethanol solvent to water increases as the ionization potential of the amine group decreases and/or the electron affinity of

the naphthalene ring increases. These effects are general and cannot be attributed to specific quenching or association effects with the solvent. (2) Since the solvent-dependent spectral shifts of the lowest energy absorption bands are smaller in magnitude than those in the fluorescence spectra and since the fluorescence
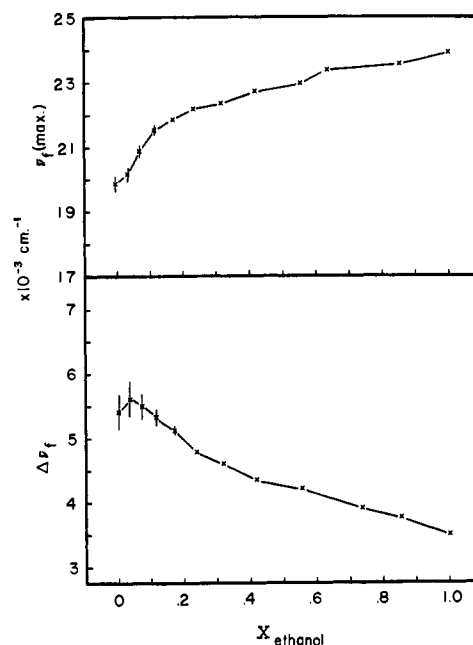

Figure 4. Fluorescence maxima and bandwidths of N-phenyl-2-aminonapththalene-6-sulfonate as a function of the mole fraction of ethanol in ethanol–water mixtures.

energy *decreases* in going from ethanol to water, it can be concluded that $\mu(S_1) > \mu(S_0)$.

The effects of the solvent dielectric constant on the energies and bandwidths of fluorescence were measured in ethanol–water solvent mixtures. Plots of the energies and bandwidths vs. the mole fraction of ethanol were constructed. Typical results are shown in Figures 3
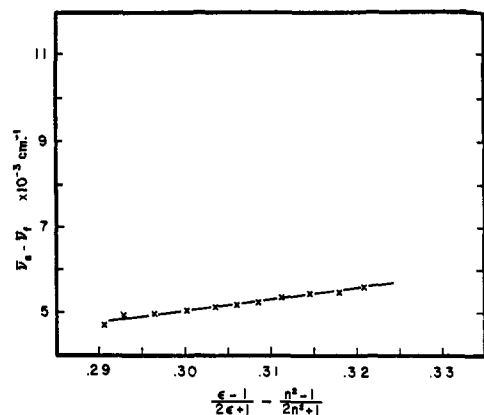
Figure 5. Plot of the Stokes shift of 2-aminonaphthalene-6-sulfonate vs. the dielectric constant and refractive index term for ethanol–water mixtures.
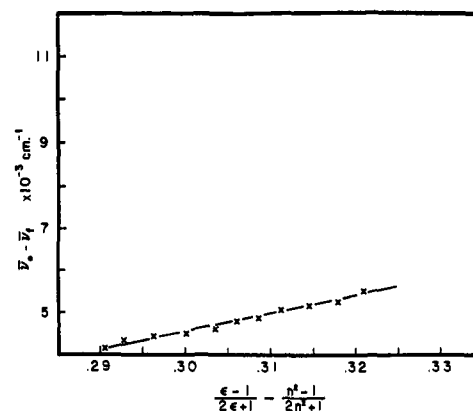

Figure 6. Plot of the Stokes shift of N-cyclohexyl-2-aminonaphthalene-6-sulfonate vs. the dielectric constant and refractive index term for ethanol–water mixtures.

and 4. The estimated errors for both $\Delta\bar{\nu}_f$ and $\bar{\nu}_f$ are indicated by vertical bars. Where no error bars are present the errors were estimated to be ± 100 cm^{-1} for $\Delta\bar{\nu}_f$ and ± 50 cm^{-1} for $\bar{\nu}_f$.

The energies of fluorescence for all the derivatives increased as the mole fraction of ethanol was increased. Each curve of $\bar{\nu}_f$ vs. the ethanol mole fraction was similar in shape, suggesting that the energies varied in a similar way for all of the molecules.

The bandwidth data showed, in general, that there was an increase in $\Delta\bar{\nu}_f$ as the static dielectric constant was increased. However, anomalous behavior was found for the N-arylaminonaphthalene-6-sulfonates at low mole fractions of ethanol. Since the errors in the determination of the bandwidths are very large at low ethanol mole fraction values, it cannot be certain that the decreases indicated are significant. They may be artifacts of the large spectral correction factors and very low light intensities encountered.

Comparison of the fluorescence energies, bandwidths, and quantum yields in ethanol and water and their solvent mixtures leads to the following conclusions. (1) The magnitudes of the observed effects were smooth functions of the mole fractions of ethanol except for possibly the bandwidths at very low ethanol mole fraction values. (2) The magnitude of the overall effects increased as the amine group was substituted with groups of lower ionization potential and/or as the electron affinity of the naphthalene ring was increased by the addition of the sulfonate group. (3) The behavior of the fluorescence energies, bandwidths, and quantum yields are related. That is, the energies decreased, the bandwidths increased, and the quantum yields decreased as the dielectric constant of the solvent increased.

Several theories have been advanced to account for the solvent dependence of the fluorescence energies of molecules whose electronic transitions are similar to those discussed here.[8–10] The results of Lippert[9] and

$$\bar{\nu}_A - \bar{\nu}_f \approx \frac{2}{hc_0}\left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) \times$$
$$\left(\frac{(\mu_e - \mu_g)^2}{a^3}\right) + \text{constant} \quad (1)$$

(8) N. Mataga, Y. Keifu, and M. Koizumi, *Bull. Chem. Soc. Jap.*, **29**, 465 (1956).
(9) E. Lippert, *Z. Naturforsch. A*, 10, 541 (1955).
(10) L. Bilot and A. Kawski, *ibid.*, *A*, **18**, 10, (1963).

Mataga, et al.,[8] are essentially the same. Thus eq 1 was obtained where the terms are defined as follows: $\bar{\nu}_a$ is the wavenumber (cm^{-1}) of the lowest energy singlet absorption maximum, $\bar{\nu}_f$ is the wavenumber (cm^{-1}) of the fluorescence maximum, h is Planck's constant, c_0 is the speed of light in a vacuum, ϵ is the static dielectric constant of the solvent, n is the refractive index of the solvent, μ_e is the dipole moment of the first excited singlet state of the solute, μ_g is the dipole moment of the ground singlet state of the solute, and a is the radius of the Onsager cavity for the solute molecule in question.

The Onsager cavity radii for the molecules in this study were estimated by comparing the actual molecular sizes of the molecules. The conclusions drawn from the results of using the above equation depend only on their relative values. However, the values obtained for $(\mu_e - \mu_g)$ here may differ from the actual values by as much as 50%.

From each of the curves of $\bar{\nu}_f$ vs. the mole fraction of ethanol values for the Stokes shift, $\bar{\nu}_a - \bar{\nu}_f$, and the term in the above equation containing the dielectric constant and refractive index could be obtained. Since the energy of the lowest absorption maximum, $\bar{\nu}_a$, changes very little relative to the fluorescence maximum, $\bar{\nu}_f$, in going from ethanol to water, the values of the absorption maximum in ethanol were used in the calculations. Typical plots of the data according to the above equation are given in Figures 5 to 7. The experimental data determine straight lines within the limits of the error and the nonideality of the behavior of the solvent mixtures. The differences in the electric dipole moments, $\mu_e - \mu_g$, were computed by measuring the slopes of these graphs. The values obtained are presented in Table II along with the assumed Onsager radii. As before, the ordering of the molecules in this table represents that expected for the decrease in the ionization potential of the amine group and/or the increase of the electron affinity of the naphthalene ring. We have also reevaluated the data of Turner and Brand[6] for the 1-substituted N-arylaminonaphthalenesulfonates and find that the behavior of the fluorescence of these molecules conforms well with the analysis advanced in this report.

The small changes in the lowest energy absorption maxima, $\bar{\nu}_a$, relative to the fluorescence maxima, $\bar{\nu}_f$, for the series of molecules in this study indicate that the dipole moments of the ground singlet states, μ_g, are
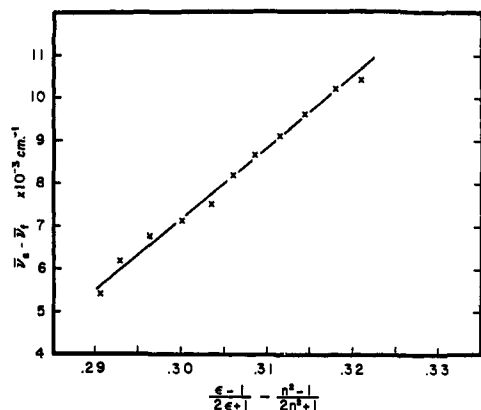
Figure 7. Plot of the Stokes shift of N-phenyl-N-methyl-2-amino-naphthalene-6-sulfonate $vs.$ the dielectric constant and refractive index term for ethanol–water mixtures.

Figure 8. Fluorescence spectra of N-phenyl-N-methyl-2-amino-naphthalene-6-sulfonate in glycerol at 300°K (———) and at 320°K (– – – –).

small relative to those of the first excited singlets, μ_e. Thus, the computed values of $\mu_e - \mu_g$ largely reflect the changes in μ_e when comparing one molecule to another. The magnitudes of the dipole moment changes in Table II are unusually large. However, only the relative behavior from molecule to molecule is considered here.

Table II. Calculated Dipole Moment Changes in Ethanol–Water Mixtures

Molecule	Onsager radius, Å	$\mu_e - \mu_g$, D
2-Aminonaphthalene-6-sulfonate	3	9
N,N-Dimethyl-2-aminonaphthalene-6-sulfonate	4	19
N-Phenyl-2-aminonaphthalene	4	20
N-Cyclohexyl-2-aminonaphthalene-6-sulfonate	5	23
N-Phenyl-2-aminonaphthalene-6-sulfonate	5	40
N-Phenyl-N-methyl-2-aminonaphthalene-6-sulfonate	5	46
N-(o-Tolyl)-2-aminonaphthalene-6-sulfonate	5	49
N-(m-Tolyl)-2-aminonaphthalene-6-sulfonate	5	42
N-(p-Tolyl)-2-aminonaphthalene-6-sulfonate	5	44

From the results of Table II the following conclusions may be drawn. (1) The electric dipole moments of the first excited singlet states of these molecules increased in nearly the same order as that found for the decrease in the ionization potential of the amine group and/or the increase of the electron affinity of the naphthalene ring system. (2) The changes in the electric dipole moments, $\mu_e - \mu_g$, of all the N-arylaminonaphthalenesulfonate derivatives were about four times that of the parent molecule 2-aminonaphthalene-6-sulfonate.

The description of the ground and first excited singlet states is now more clear. For any given molecule, the ground singlet electric dipole moment is smaller than that for the first excited singlet. This is a result of the $a_\pi \leftarrow 1$ intramolecular charge-transfer character in the lowest energy transition. In addition, the magnitudes of the changes in the fluorescence parameters, including the decreases in the absolute quantum yields, correlated well with the increases in the dipole moments of the first excited singlet states of these molecules.

Solvent relaxation has been shown to be a key factor in the determination of the absorption and fluorescence parameters for several molecules that exhibit large dipole moment changes in their singlet states.[11] Since
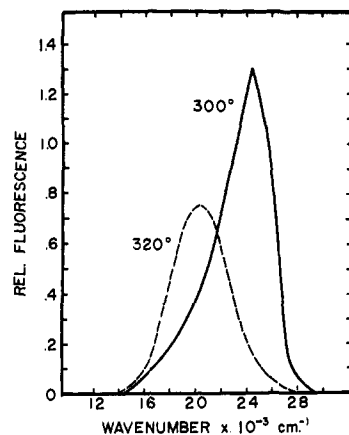
the calculated values of the changes in the dipole moments of the molecules studied here indicated that those of the first excited singlet states were larger than those of the ground state, the luminescence of one of these derivatives was studied under conditions where solvent relaxation could not occur during the lifetime of the first excited singlet state.

The relaxation time of glycerol at 300°K is of the order of nanoseconds.[12] For this solvent small changes in the temperature result in large changes in the molecular relaxation time. Since the fluorescence lifetimes of the N-arylaminonaphthalenesulfonates are also of the order of nanoseconds,[13] one might expect to find large changes in the fluorescence parameters of these molecules over a small temperature interval. Such changes were found for N-phenyl-N-methyl-2-aminonaphthalene-6-sulfonate. The corrected fluorescence spectra of this molecule at 300°K and 320°K are shown in Figure 8. The shapes and heights of the two curves are to scale relative to one another. Thus the areas under the two emission spectra give the relative quantum yields. A calculation of the relative quantum yields for these two spectra showed that the absolute yield at 300°K was about 1.6 times greater than that at 320°K. The half-maximum bandwidth at 300°K was more than 1200 cm^{-1} smaller than that at 320°K. The decrease in the energy of the fluorescence maximum was about 4000 cm^{-1} at 320°K with reference to that at 300°K. At 300°K in glycerol a hint of vibrational fine structure appeared in the fluorescence suggesting that solvent–solute interaction during the first excited singlet state of the solute affects the band shape. There were no changes in the absorption spectrum of this molecule for the temperatures in question. No concentration dependence for the phenomenon was found. Similar experiments using other glycols as solvents and glycol–water mixtures results in the same type of spectral shifts observed in glycerol. For all the solvents tested the spectral shifts occurred in the temperature ranges where solvent relaxation times were expected to be of the order of nanoseconds.[12]

(11) E. Lippert in "Optische Anregung Organischer Systeme," Verlag Chemie, Weinheim, West Germany, 1966, p 342.
(12) J. G. Powles in "Molecular Relaxation Processes," Academic Press, New York, N. Y., 1966, p 127.
(13) R. F. Chen, G. G. Vurek, and N. Alexander, $Science$, 156, 949 (1967).

Preliminary results with several other molecules in various solvents showed a good correlation between the temperature dependent fluorescence shifts and the molecular relaxation time of the solvent. It was also found that the magnitude of the fluorescence shifts correlated well with the estimated changes in the dipole moments between the ground and first excited singlet states.

In summary, in all the cases studied there was an excellent correlation between the *solvent relaxation process* and the fluorescence parameters of the molecules.

The fluorescence spectra of anhydrous crystals of the N-arylaminonaphthalenesulfonate derivatives at 300°K showed a striking resemblance to those in ethanol at 300°K. The fluorescence of a hydrated crystal of N-(p-tolyl)-2-aminonaphthalene-6-sulfonate was recently reported.[14] Hydration of the crystal resulted in a lowering of the fluorescence energy and an increase in the bandwidth. These results are in accord with those presented here.

The experimental evidence presented so far may be summarized as follows. (1) In general, for the series of molecules studied, the dipole moments of both the ground and first excited singlet states increased as the ionization potentials of the amine groups decreased and/or the electron affinities of the naphthalene ring systems increased. (2) For any one molecule the dipole moment of the first excited singlet was greater than that of the ground singlet state; this was the result of the nature of the $a_\pi \leftarrow 1$ electronic transition. (3) The dipole moments of the first excited singlet states of the N-arylaminonaphthalenesulfonates were much greater than their corresponding ground-state moments. (4) The mechanism of the sensitivity of the fluorescence parameters of the solute to the solvent dielectric constant most probably involves relaxation of the solvent molecules during the lifetime of the first excited singlet state of the solute. (5) The magnitude of the sensitivity of the fluorescence parameters to solvent relaxation and the solvent static dielectric constant at 300°K correlated well with the magnitude of the dipole moment of the first excited singlet state. (6) Solvent relaxation during the lifetime of the first excited singlet state appears to be a key factor in the sensitivity of the fluorescence parameters of N-arylaminonaphthalenesulfonates to solvent "polarity."

Since the first excited and ground singlet states of all the derivatives in this study display different electric dipole moments and, thus, different percentages of charge-transfer character, the equilibrium solvent shell around the dissolved molecules would be expected to be different for the two states. Because of the relative sizes of these moments, the solute–solvent interaction energy will be greater in the first excited singlet than in the ground singlet state of any given molecule.

Since solvent shifts in the fluorescence spectra of the order of 4000 cm^{-1} were observed for the N-arylaminonaphthalenesulfonates, the location as well as the determination of the dipole moment of the triplet state, T_1, becomes of crucial importance. Unfortunately, no direct evidence for the triplet state in *liquid* solutions could be obtained. However, sufficient evidence for the nature of the triplet state in these molecules may re-

side in the work of Jackson and Porter.[15] For 2-aminonaphthalene and N,N-dimethyl-2-aminonaphthalene in aqueous solution, these investigators found the triplet state pK to be intermediate between those of the ground and first excited singlet states. Although the amounts of intramolecular charge-transfer character in the analogous states of 2-aminonaphthalene-6-sulfonate and its derivatives are undoubtedly larger, the same relative behavior of the pK values would be expected. It is assumed that the pK values reflect the relative dipole moments in their respective electronic states.[15,16] Therefore

$$\mu(S_1) > \mu(T_1) > \mu(S_0)$$

where $\mu(j)$ represents the electric dipole moment for the jth electronic state.

As a consequence of the relative sizes of the dipole moments of these three states, the solvent–solute interaction energies at *equilibrium* in each state would result in

$$\Delta E(S_1) > \Delta E(T_1) > \Delta E(S_0)$$

where $\Delta E(j)$ denotes the lowering of the solute energy as a result of interaction with the solvent.

Since the dipole moment of the first excited singlet state is much larger than that of the ground state for the N-arylaminonaphthalenesulfonates, large decreases in the fluorescence energies were found on increasing the dielectric constant of the solvent medium. For the remainder of the molecules in this study, analogous results were found except that the energy changes were smaller due to their smaller dipole moments.

The increased dipole moment of the excited state results in formation of excited Franck–Condon states which are not only out of equilibrium with respect to their zero-level vibronic states but also with respect to their solvent shells. The energy difference between the first excited singlet states just before photon emission but after solvent relaxation has occurred would be decreased by two factors: first the solvation of the excited state and, second, the supersolvation of the ground state.

Since the dipole moment of the triplet state would be intermediate between those of the two singlets in question, the separation of the first excited singlet and triplet states at equilibrium solvent reorientation would decrease due to solvent relaxation. As is the case with the lowest energy transition in the singlet manifold, intersystem crossing from the first excited singlet to the triplet state would be from a state in near solvent shell equilibrium to a supersolvated triplet state. Therefore, in liquid polar solvents with molecular relaxation times of 10^{-12} sec or less the actual S_1–T_1 energy interval of the solute could decrease to a very small value.

Since the triplet states of these compounds have been measured in rigid glasses, the energies of the T_1 states so obtained probably represent those solvated relative to the ground state (*cf.* paper I in this series). However, if the triplet state dipole moment is considerably smaller than that of the first excited singlet, the energy level of the triplet would not change much as a function of the static dielectric constant in a fluid

(14) A. Camerman and L. H. H. Jensen, *J. Amer. Chem. Soc.*, **92**, 4200 (1970).

(15) G. Jackson and G. Porter, *Proc. Roy. Soc., Ser. A*, **260**, 13, (1961).

(16) K. Kimura and H. Tsubomura, *Mol. Phys.*, 11, 349 (1966).

Table III. The Fluorescence Maxima in Water at 300°K, the Phosphorescence Maxima in Ethanol at 77°K, and the Singlet–Triplet Interval

Molecule	$\bar{\nu}_f$, cm^{-1}	$\bar{\nu}_p$, cm^{-1}	$\bar{\nu}_f - \bar{\nu}_p$, cm^{-1}
2-Aminonaphthalene-6-sulfonate	23,700	18,200	5500
N,N-Dimethyl-2-aminonaphthalene-6-sulfonate	22,420	18,200	4200
N-Phenyl-2-aminonaphthalene	22,200 ± 200	18,500	3700
N-Cyclohexyl-2-aminonaphthalene-6-sulfonate	22,750	18,600	4200
N-Phenyl-2-aminonaphthalene-6-sulfonate	19,800 ± 500	18,400	1400
N-Phenyl-N-methyl-2-aminonaphthalene-6-sulfonate	18,400 ± 500	18,400	~0
N-(o-Tolyl)-2-aminonaphthalene-6-sulfonate	19,200 ± 500	18,300	900
N-(m-Tolyl)-2-aminonaphthalene-6-sulfonate	18,400 ± 500	18,400	~0
N-(p-Tolyl)-2-aminonaphthalene-6-sulfonate	19,400 ± 500	18,700	700

medium over and above that due to supersolvation. Thus, it is probably reasonable to compare the energies of the triplet states obtained in rigid glasses with the fluorescence energies in water at 300°K. The fluorescence and phosphorescence data are shown in Table III.
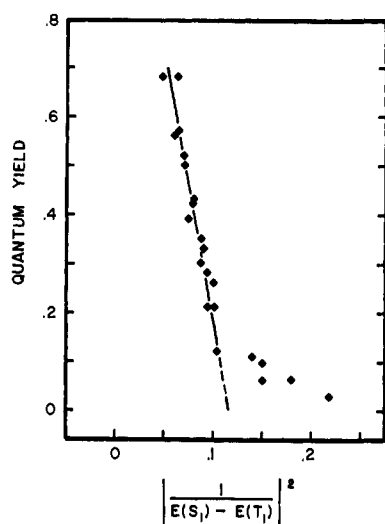

Figure 9. Plot of the absolute fluorescence quantum yield of N-phenyl-1-aminonaphthalene-7-sulfonate in organic solvent–water mixtures vs. the square of the inverse of the singlet–triplet interval.

Although it is certain that the values of the S_1-T_1 intervals calculated in this manner are not exactly those occurring in fluid polar solvents, these intervals represent the phenomenon that is occurring. It will be recalled that the fluorescence quantum yields in water decreased in roughly the same order as the S_1-T_1 interval decreased. From quantum mechanical perturbation theory, one expects transition probabilities between close-lying states to be roughly proportional to the square of the inverse of the energy interval between the two states. In that regard the quantum yields and emission maxima determined for N-phenyl-1-amino-

naphthalene-7-sulfonate by Turner and Brand[6] have been reexamined. A plot of the absolute fluorescence quantum yield vs. the reciprocal of the square of the energy difference between the fluorescence and phosphorescence maxima should be roughly linear. Since the phosphorescence maxima of nearly all of the N-arylaminonaphthalenesulfonates in this study were about 18,300 cm^{-1}, this value was assumed for N-phenyl-1-aminonaphthalene-7-sulfonate. The results are shown in Figure 9. The plot shows the relationship to be linear over 80% of the ordinate axis. At low quantum yields and low fluorescence energies, the calculation of the singlet–triplet split is very sensitive to any errors in determining $\bar{\nu}_f$ and $\bar{\nu}_p$. The results of this graph constitute a further proof of the validity of the interpretations advanced in this report for the luminescence behavior of the N-arylaminonaphthalenesulfonates.

Conclusions

The consequences of the results and discussion presented may be summarized as follows. (1) Solvent relaxation during the lifetime of the first excited singlet states of molecules with $a_\pi \leftarrow 1$ intramolecular charge-transfer transitions would be expected to decrease the S_1-T_1 interval and therefore increase the probability of intersystem crossing. (2) For the series of molecules in this study, as the ionization potential of the amine group was decreased and/or as the electron affinity of the naphthalene ring system was increased, the S_1-T_1 interval would be expected to decrease in liquid polar solvents due to solvent relaxation. (3) The low fluorescence quantum yields of the N-arylaminonaphthalenesulfonates in liquid polar solvents can be explained by a large increase in intersystem crossing due to solvent relaxation during the lifetime of the first excited singlet state.[17]

(17) NOTE ADDED IN PROOF. Since this manuscript was submitted for publication, additional evidence for solvent relaxation during the first excited singlet lifetime of N-(p-tolyl)-2-aminonaphthalene-6-sulfonate has been obtained using nanosecond fluorometry: L. Brand and U. R. Gohlke, J. Biol. Chem., 246 2317 (1971). Similar data have been obtained with N-phenyl-1-aminonaphthalene-8-sulfonate by W. R. Ware, et al., unpublished results.