salicylanils.[10] A more detailed discussion of the fluorescence will appear in a future communication.

Acknowledgments. L. H. Vogt would like to thank Dr. J. S. Kasper for the use of his Datex atuomated G. E. diffractometer.

[10] W. F. Richey and R. S. Becker, *J. Chem. Phys.*, **49**, 2092 (1968).

Electronic Spectra of 2-Aminonaphthalene-6-sulfonate and Related Molecules. I. General Properties and Excited-State Reactions[1]

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 absorption and luminescence spectra of 2-aminonaphthalene-6-sulfonate and its derivatives suggest the importance of intramolecular charge transfer in the spectral properties of these molecules. The lone-pair electrons on the nitrogen atom are principally involved in the lower energy electronic transitions in all of these molecules, and this suggests that the two lowest energy absorptions can be assigned as $a_\pi \leftarrow l$ transitions. The excited-state reactions of 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate are presented and rationalized on the basis of the $a_\pi \leftarrow l$ transition.

Substituted naphthalene derivatives have been used as fluorescence probes to obtain information about enzymes,[3] mitochondrial membranes,[4] and nerve excitation.[5] Interpretation of fluorescence changes related to biological function requires an understanding of the excited states involved. The aim of this research was a partial characterization of the lower electronic states of a series of 2-aminonaphthalene-6-sulfonate derivatives.

The spectroscopy of these molecules is of interest in its own right. The low-energy electronic transitions in aromatic amines, especially aniline, have been interpreted in terms of a "composite molecule" approach.[6–8] In this theory, aromatic hydrocarbons having strongly conjugating groups, such as an amine, are treated as being made up of two component molecules. The electronic states of the whole molecule would then be some combination of the local states of both parts *plus* a certain percentage of electron-transfer states between the two components. In the case of the anilines the theory has been worked out extensively[9–12] and Kimura, *et al.*,[13,14] have obtained experimental results that agree well with theoretical predictions. The discussion of the electronic states of 2-aminonaphthalene-6-sulfonate and its derivatives studied here will be treated in the general terms of this theory.

Experimental Section

Solvents. *tert*-Butyl alcohol was obtained from Matheson Coleman and Bell and redistilled through a 40-cm Vigreux column. The middle fraction boiling at 82 ± 0.5° was collected and used.

Absolute ethanol was obtained from Publicker Industries, Inc. (Philadelphia, Pa.), and used as such for all the fluorescence measurements at 300°K. No significant fluorescence was observed from the solvent itself. Ethanol used for the measurements of fluorescence and phosphorescence at 77°K was refluxed for more than 3 hr over metallic magnesium and then distilled through a 38-cm column of Rhashig rings. The middle fraction boiling at 78 ± 0.5° was collected and immediately used. Absolute ethanol treated in this manner formed crack-free glasses at 77°K. Water was either distilled from an alkaline permanganate solution and then again, or processed by a Hydro, Inc., water processing unit. In either case no fluorescence or significant ultraviolet absorption could be detected from pure water above 2000 Å.

Aqueous solutions of acids were obtained by diluting commercially available reagents (Baker Chemical Co.). Solid sodium and potassium hydroxides were obtained from Baker Chemical Co., and their solutions were prepared gravimetrically.

Aqueous solutions of the compounds studied here containing dissolved oxygen showed no increase in their fluorescence quantum yields after outgassing with pure nitrogen gas. However, when these molecules were dissolved in more nonpolar solvents, such as ethanol, increased fluorescence yields were found after outgassing with dry nitrogen gas. However, there were no changes in the shapes of the emission bands after outgassing any of the solvents. Thus, fluorescence quantum yields in organic solvents were measured only after outgassing to maximum quantum yield with ultrapure dry nitrogen gas (Air Products, Baltimore, Md.), whereas energies and bandwidths of emission were determined on air-equilibrated solutions.

Organic Syntheses and Purifications. The following compounds were used in this study.

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[1] Contribution No. 644 from the McCollum–Pratt Institute. This research was supported by NIH Grant No. G. M. 11632. A preliminary account of this work has appeared in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969.

[2] Based in part on a thesis submitted by C. J. S. in partial fulfillment of the requirements for the degree Doctor of Philosophy at The Johns Hopkins University.

[3] G. M. Edelman and W. O. McClure, *Accounts Chem. Res.*, **1**, 65 (1968).

[4] A. Azzi, B. Chance, G. K. Radda, and C. P. Lee, *Proc. Nat. Acad. Sci. U. S.*, **62**, 612 (1969).

[5] I. Tasaki, R. Wantanabe, R. Sandlin, and L. Carnay, *ibid.*, **61**, 883 (1968).

[6] J. N. Murrell, *Proc. Phys. Soc., London, Sect. A*, 68, 969 (1955).

[7] H. C. Longuet-Higgins and J. N. Murrell, *ibid.*, *Sect. A*, **68**, 601 (1955).

[8] S. P. McGlynn, L. Vanquickenborne, M. Kinoshita, and D. G. Carroll, "Introduction to Applied Quantum Chemistry," Holt, Rinehart and Winston, New York, N. Y., in press.

[9] E. C. Lim and S. K. Chakrabarti, *J. Chem. Phys.*, **47**, 4726 (1967).

[10] M. Godfrey and J. N. Murrell, *Proc. Roy. Soc., Ser. A*, **278**, 57 (1964).

[11] M. Godfrey and J. N. Murrell, *ibid.*, *Ser. A*, **278**, 64 (1964).

[12] M. Godfrey and J. N. Murrell, *ibid.*, *Ser. A*, **278**, 71 (1964).

[13] K. Kimura, H. Tsubomura, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **37**, 1336 (1964).

[14] K. Kimura and H. Tsubomura, *Mol. Phys.*, **11**, 349 (1966).

Naphthalene-2-sulfonate (sodium salt) was obtained from Aldrich Chemical Co. (Milwaukee, Wis.) and first recrystallized from an aqueous solution of sodium bisulfite (1.4 *M*) and sodium sulfite (0.08 *M*). White crystalline plates of naphthalene-2-sulfonate were obtained after three more crystallizations from water.

2-Aminonaphthalene was purchased from Aldrich Chemical Co. and recrystallized two times from absolute ethanol.

2-Aminonaphthalene-6-sulfonate (sodium salt) was obtained from Aldrich Chemical Co. and first recrystallized from sulfite–bisulfite solution and then four times from water.

***N*-Phenyl-2-aminonaphthalene** was obtained from Aldrich Chemical Co. and recrystallized four time from absolute ethanol.

***N*-(*p*-Hydroxyphenyl)-2-aminonaphthalene** was obtained from Aldrich Chemical Co. and recrystallized eight times from cyclohexane solutions containing a trace of ethanol.

Di-2-naphthylamine was obtained from Aldrich Chemical Co. and recrystallized three times from acetone.

***N*,*N*-Dimethyl-2-aminonaphthalene-6-sulfonate** (sodium salt) was synthesized according to a procedure outlined by Laurence[15] and recrystallized three times from water.

***N*-Phenyl-*N*-methyl-2-aminonaphthalene-6-sulfonate** (sodium salt) was synthesized according to the procedure of Cory, *et al.*,[16] and twice recrystallized from water.

***N*-Phenyl-2-aminonaphthalene-6-sulfonate** (sodium salt) was synthesized from the starting materials prescribed by Bucherer and Stohmann.[17]

***N*-Cyclohexyl-2-aminonaphthalene-6-sulfonate** (sodium salt) was synthesized by a method similar to that for *N*-phenyl-2-aminonaphthalene-6-sulfonate. The sodium salt was prepared by first making the sulfonic acid in 1 *N* HCl and then recrystallizing the resulting precipitate from dilute NaOH solution. A final recrystallization from water yielded white crystalline plates.

***N*-(*o*-Tolyl)-2-aminonaphthalene-6-sulfonate** (sodium salt) was synthesized from the starting materials prescribed by Bucherer and Stohmann.[17] Recrystallization of the product from sulfite–bisulfite solution, and then four times from water resulted in a pure compound.

***N*-(*m*-Tolyl)-2-aminonaphthalene-6-sulfonate** (sodium salt) was synthesized from the starting materials prescribed by Bucherer and Stohmann.[17] Recrystallization from sulfite–bisulfite solution and then three times from water yielded white crystalline plates.

***N*-(*p*-Tolyl)-2-aminonaphthalene-6-sulfonate** (sodium salt) was synthesized from the starting materials prescribed by Bucherer and Stohmann.[17] Recrystallization from sulfite–bisulfite solution and then twice from water yielded white crystalline plates.

All of the above compounds that were crystallized from aqueous solutions were dried for several days over phosphorus pentoxide (Baker Chemical Co.) under reduced pressure. These compounds were tested for homogeneity by thin-layer chromatography on silica gel (Eastman 6060 and 6061). Two solvent systems were used: first, butanol–acetic acid–water (50/12/50) and, secondly, benzene. None of the compounds described above contained any detectable contaminant except possibly *N*-(*p*-hydroxyphenyl)-2-aminonaphthalene. The latter compound showed a trace of a nonfluorescent compound which appeared to be an artifact of the chromatography. Fresh solutions of *N*-(*p*-hydroxyphenyl)-2-aminonaphthalene did not contain a significant amount of the reddish colored contaminant.

Absorption Spectra. Absorption spectra were recorded on a Cary 14M spectrophotometer.

Oscillator Strengths and Calculated Lifetimes. The oscillator strengths of the two lowest energy absorptions were computed by estimating the area under symmetrical curves fitted to the absorption spectra. The curves were constructed by estimating the absorption maximum of the lowest energy band and then proceeding from lower to higher energies, drawing the mirror image curves. In this manner two symmetrical curves were obtained that approximated the absorption spectrum well. It was estimated that oscillator strengths of the lowest energy absorption band could be obtained within an error of ±10%. Computations of the oscillator strengths for the second absorption bands were made more difficult by the presence of overlapping bands. It was estimated that the error here was on the order of ±30%.

Fluorescence lifetimes were calculated by using a modification of the equation of Strickler and Berg.[18] The resolved lowest energy bands determined by the method given above were used to compute the lifetimes.

Luminescence Spectra. Fluorescence spectra were measured on the instument described by Witholt and Brand.[19] Phosphorescence spectra were recorded on an Aminco-Keirs spectrophosphorimeter using a quartz dewar–cold finger assembly. In all cases the emissions from quartz or solvents alone were insignificant. All the luminescence spectra have been corrected for the spectral responses of the photomultiplier phototubes and emission monochromators.

The quantum yield of fluorescence, Ω_u, of a solution of a molecule u, dissolved in a solvent of refractive index n_u, and whose transmittance at λ_u is T_u, is given by

$$\Omega_u = \Omega_k \frac{{n_u}^2}{{n_k}^2}\frac{1 - T_k}{1 - T_u}\frac{\int F_u \mathrm{d}\lambda}{\int F_k \mathrm{d}\lambda} \qquad (1)$$

where Ω_k is the quantum yield of a reference molecule, k, dissolved in a solvent of refractive index n_k and whose solution has a transmittance of T_k at wavelength λ_u ($\lambda_u = \lambda_k$); F_u and F_k are *corrected* fluorescence spectra of the solutions of molecules u and k, respectively.

Relative quantum yields of fluorescence were computed by numerically integrating the areas under the emission curves of both the reference and sample molecules and then substituting these values into the equation for Ω_u above. Quinine sulfate dissolved in 0.1 *N* H_2SO_4 was used as a standard; its quantum yield was taken as 0.55 while exciting the fluorescence at 3500 Å.[20,21] Quinine sulfate was obtained from Mallinckrodt Chemical Co. and used without further purification. For determinations of relative quantum yields of fluorescence the transmittances T_u and T_k were both kept above 0.80 in order to minimize inner-filter effects.

Acidity Measurements and Titrations. Acidity measurements were taken with either a Beckman Zeromatic (Beckman electrode 39030) or a Beckman Model G (Beckman electrodes 39270 and 40208) pH instrument. Both instruments gave identical results within the limits of experimental accuracy (±0.05 pH unit) over the range $0 \leq \text{pH} \leq 12.5$.

Measurements of fluorescence emission spectra of a given compound taken during pH titrations in cases where changes in the absorption spectrum occurred were carried out by exciting the fluorescence at an isosbestic point for the changes that occurred in the absorption spectrum.

Results and Discussion

Spectroscopic Properties in Ethanol. The absorption, fluorescence, and phosphorescence spectra of 2-aminonaphthalene-6-sulfonate and its derivatives have several common features. Typical spectra are shown in Figures 1–4. The two lowest energy absorption bands are similar in shape and relative intensity for all the molecules. (The second absorption band of 2-aminonaphthalene is present as a shoulder on the low-energy side of the band observed at 34–36 × 10^3 cm^{-1}.) Thus, the amino group can produce the two broad-banded, lower energy absorptions spaced about 4000 cm^{-1} apart common to all these molecules. These two bands are in striking contrast to the two lowest energy absorptions in either naphthalene or naphthalene-2-sulfonate since these two molecules have very similar spectra.

Since the lowest energy absorption usually gives rise to its corresponding fluorescence, measurement of the oscillator strength of this absorption band permits an estimate of the fluorescence lifetime in the absence of external quenching agents.[18] The oscillator strengths[22] and energies for the first two transitions, the values of

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(15) D. J. R. Laurence, *Methods Enzymol.*, **4**, 174 (1957).

(16) R. P. Cory, R. R. Becker, R. Rosenbluth, and I. Isenberg, *J. Amer. Chem. Soc.*, **90**, 1643 (1968).

(17) H. Bucherer and A. Stohmann, *Chem. Zentralbl.*, **75**, 1012 (1904).

(18) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

(19) B. Witholt and L. Brand, *Rev. Sci. Instrum.*, **39**, 1271 (1968).

(20) J. W. Eastman, *Photochem. Photobiol.*, **6**, 55 (1967).

(21) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).

(22) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, p 358.

Table I. Energies, Oscillator Strengths, and Transition Moments in Ethanol

Molecule	$\bar{\nu}_{S_1\leftarrow S_0}$, cm^{-1} ± 200	$f_{S_1\leftarrow S_0}$ ± 10%	$\bar{\nu}_{S_2\leftarrow S_0}$, cm^{-1} ± 400	$f_{S_2\leftarrow S_0}$ ± 30%	$\frac{f_{S_2\leftarrow S_0}}{f_{S_1\leftarrow S_0}}$	$\left\lvert\frac{M^{el}_{S_1\leftarrow S_0}}{e}\right\rvert^2$, (Å)^2	$\left\lvert\frac{M^{el}_{S_1\leftarrow S_0}}{e}\right\rvert$, Å
2-Aminonaphthalene	29,200	0.026	34,000			0.082	0.29
2-Aminonaphthalene-6-sulfonate	29,100	0.028	33,500	0.054	3.9	0.088	0.30
N-Cyclohexyl-2-aminonaphthalene-6-sulfonate	28,200	0.051	32,900	0.203	4.0	0.166	0.41
N-Phenyl-2-aminonaphthalene	28,800	0.052	32,500	0.197	3.8	0.167	0.41
Di-2-naphthylamine	28,500	0.157	31,700	0.242	1.5	0.508	0.72
N-(*p*-Hydroxyphenyl)-2-aminonaphthalene	28,000	0.043	32,800	0.240	5.6	0.141	0.38
N-Phenyl-2-aminonaphthalene-6-sulfonate	28,600	0.118	31,900	0.351	3.0	0.381	0.62
N-Phenyl-*N*-methyl-2-aminonaphthalene-6-sulfonate	28,300	0.057	31,900	0.227	4.0	0.186	0.43
N-(*o*-Tolyl)-2-aminonaphthalene-6-sulfonate	28,600	0.071	32,100	0.241	3.4	0.229	0.48
N-(*m*-Tolyl)-2-aminonaphthalene-6-sulfonate	28,400	0.106	31,700	0.315	3.0	0.344	0.59
N-(*p*-Tolyl)-2-aminonaphthalene-6-sulfonate	28,000	0.070	31,500	0.250	3.6	0.230	0.48

$M^{el}_{S_1\leftarrow S_0}/e$, the transition moment, and the calculated fluorescence lifetimes are given in Tables I and II. The calculated lifetimes have also been adjusted for their actual quantum yields of fluorescence. Although the interpretation for each of these molecules is not completely clear, the following generalizations may be made. First, substitution of the nitrogen atom, while keeping the remainder of the molecule constant, with more electron donating groups results in a decrease in the $S_1 \leftarrow S_0$ transition energy, an increase in the electronic transition moment, $M^{el}_{S_1\leftarrow S_0}/e$, and a decrease in the natural fluorescence lifetime, τ_0. Second, it generally holds that the energy of the $S_2 \leftarrow S_0$ transition decreases as the ionization potential of the amine group is decreased, although the exceptions to this rule are more frequent. The ratio of the oscillator strengths $f_{S_2\leftarrow S_0}/f_{S_1\leftarrow S_0}$ shows wide variation, for which several reasons may exist. First, the configuration of the nitrogen atom may influence the transition moments and energies of the two transitions differently. Second, owing to the overlap of neighboring absorption bands, the resolution of the second transition is more difficult than the first. Thus it cannot be certain that some of the exceptions to the rules set down above are not artifacts of the experimental procedure.

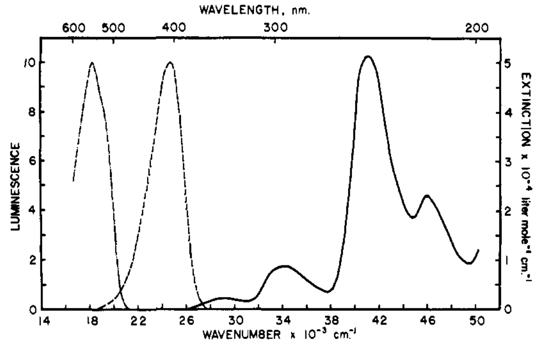

Figure 1. Luminescence and absorption spectra of 2-aminonaphthalene-6-sulfonate in ethanol: ———, molar extinction; ----, fluorescence at 300°K; —·—·—, phosphorescence at 77°K.

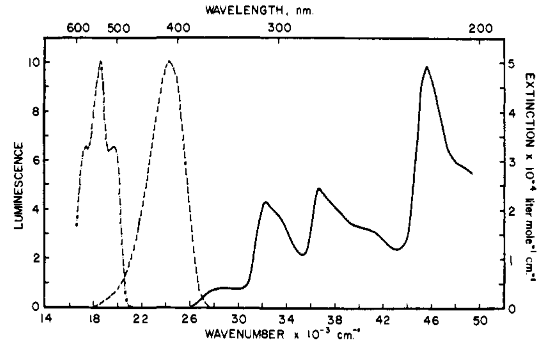

Figure 2. Luminescence and absorption spectra of *N*-phenyl-2-aminonaphthalene in ethanol: ———, molar extinction; ----, fluorescence at 300°K; —·—·—, phosphorescence at 77°K.

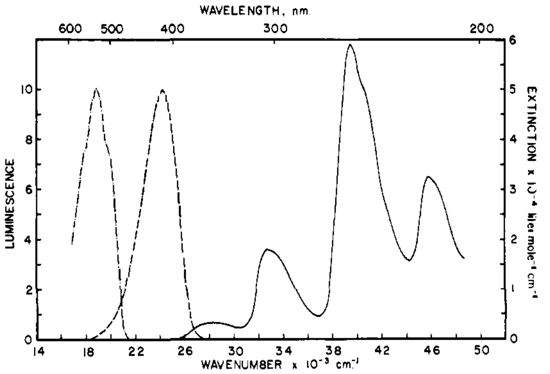

Figure 3. Luminescence and absorption spectra of *N*-cyclohexyl-2-aminonaphthalene-6-sulfonate in ethanol; ———, molar extinction: ----, fluorescence at 300°K; —·—·—, phosphorescence at 77°K.

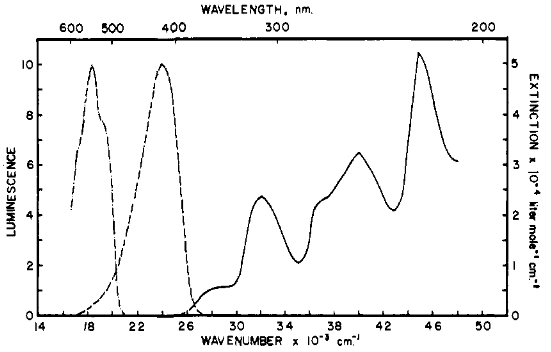

Figure 4. Luminescence and absorption spectra of *N*-(*o*-tolyl)-2-aminonaphthalene-6-sulfonate in ethanol: ———, molar extinction; ----, fluorescence at 300°K; —·—·—, phosphorescence at 77°K.

Table II. Calculated Fluorescence Lifetimes in Ethanol and Associated Parameters

Molecule	$\bar{\nu}_f$(max), cm^{-1} ± 50	Concn, *M*	$\int A(\bar{\nu})$d ln $\bar{\nu}$ × 10^3	τ_0, nsec	$\Omega_u \tau_0$, nsec
2-Aminonaphthalene	24,710	4.1×10^{-5}	10.50	48.7	28.7
2-Aminonaphthalene-6-sulfonate	24,550	2.03×10^{-5}	5.563	46.4	24.6
N-Phenyl-2-aminonaphthalene	24,350	4.31×10^{-5}	21.32	26.3	11.6
N-Cyclohexyl-2-aminonaphthalene-6-sulfonate	24,080	2.97×10^{-5}	15.06	26.6	12.2
N-(*p*-Hydroxylphenyl)-2-aminonaphthalene	20,100	4.65×10^{-5}	19.9	54.1	5.4
Di-2-naphthylamine	23,910	2.95×10^{-5}	42.28	9.60	3.26
N-Phenyl-2-aminonaphthalene-6-sulfonate	23,980	2.57×10^{-5}	29.60	11.8	7.67
N-Phenyl-*N*-methyl-2-aminonaphthalene-6-sulfonate	22,940	4.52×10^{-5}	25.11	28.0	14.0
N-(*o*-Tolyl)-2-aminonaphthalene-6-sulfonate	24,050	3.84×10^{-5}	26.64	19.5	11.1
N-(*m*-Tolyl)-2-aminonaphthalene-6-sulfonate	23,730	2.95×10^{-5}	30.77	13.5	9.32
N-(*p*-Tolyl)-2-aminonaphthalene-6-sulfonate	23,090	2.16×10^{-5}	15.02	22.0	14.7

The spectroscopic parameters of the two lowest energy singlet–singlet transitions in the aminonaphthalenesulfonate derivatives are similar to those observed for aniline and its derivatives. Aniline is thought to have significant intramolecular charge-transfer character in its two lowest energy bands, and this suggests that the same holds true for the molecules in this study.

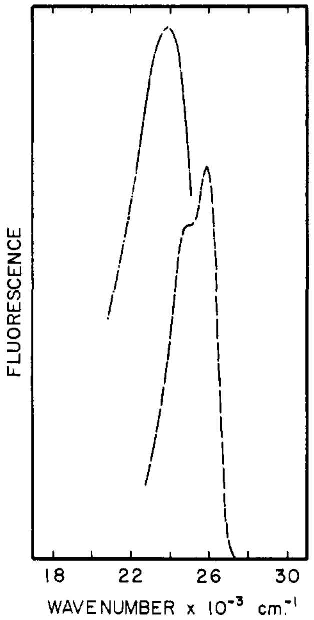

Figure 5. Fluorescence spectra of *N*-phenyl-2-aminonaphthalene (– – – –) and *N*-(*p*-hydroxyphenyl)-2-aminonaphthalene (–·–·–) in ethanol at 77°K.

The fluorescence spectra of the molecules studied here are broad and structureless in ethanol or more polar solvents at 300°K. When dissolved at 300°K in a more nonpolar solvent such as cyclohexane, a hint of fine structure begins to appear in the lowest energy absorption band and in the fluorescence spectrum. The fluorescence spectra of these molecules and, presumably, the absorption spectra, show some vibrational fine structure at 77°K in ethanol glasses. The phosphorescence also shows a good deal of fine structure at 77°K except for those molecules containing sulfonate groups. Even in these latter molecules, the vibrational structure is evident but to a lesser extent than in those molecules devoid of this group. For the sake of comparison, typical fluorescence and phosphorescence spectra in ethanol at 77°K are shown in Figures 5 and 6.

The energies and progression of vibrational bands for the phosphorescence of naphthalene are well known. The addition of the amine group, substituted or not, in the 2 position resulted in a broadening of the phosphorescence of naphthalene. The energies and bandwidths of fluorescence and the phosphorescence energies of these molecules in ethanol glasses at 77°K are given in Table III. For those compounds that contained the sulfonate group, the positions of their 0–0 bands could not be determined accurately, nor could any other vibrational bands except the maximum phosphorescence wave number.

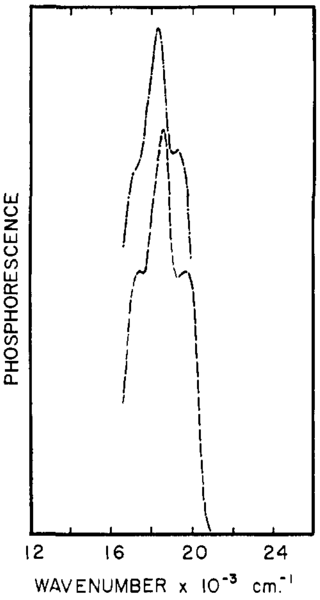

Figure 6. Phosphorescence spectra of *N*-phenyl-2-aminonaphthalene (– – – –) and *N*-(*p*-hydroxyphenyl)-2-aminonaphthalene (–·–·–) in ethanol at 77°K.

Comparisons of the shapes and energies of the fluorescence and phosphorescence spectra showed that (1) in general, the fluorescence bands have different vibrational fine structure than the corresponding phosphorescence bands; (2) the energies of the 0–0 bands of both the phosphorescence and fluorescence (or, where none can be distinguished, the emission maxima) change only slightly from compound to compound; (3) the loss of vibrational fine structure is correlated with the decrease of the ionization potential of the amine group and/or the addition of the sulfonate group; (4) in the case of *N*-(*p*-hydroxyphenyl)-2-aminonaphthalene the

Table III. Energies and Bandwidths of Fluorescence and Energies of Phosphorescence at 77°K

Molecule	$\bar{\nu}_f$(max), cm^{-1} ± 100	$\Delta\bar{\nu}_f$, cm^{-1} ± 200	$\bar{\nu}_p$, cm^{-1} ± 100: 0–0	Maximum	Other peaks
2-Aminonaphthalene-6-sulfonate	25,400	2900		18,200	
N,*N*-Dimethyl-2-aminonaphthalene-6-sulfonate	25,200	2800		18,200	
N-Phenyl-2-aminonaphthalene	25,800	2600	19,600	18,500	17,300
N-Cyclohexyl-2-aminonaphthalene-6-sulfonate	25,400	2800		18,600	
Di-2-naphthylamine	25,500	2300	19,300	18,300	17,100
N-(*p*-Hydroxyphenyl)-2-aminonaphthalene	23,700	3600	19,200	18,200	17,000
N-Phenyl-2-aminonaphthalene-6-sulfonate	25,400	2600		18,400	
N-Phenyl-*N*-methyl-2-aminonaphthalene-6-sulfonate	25,300	2900		18,400	
N-(*o*-Tolyl)-2-aminonaphthalene-6-sulfonate	25,400	2700		18,300	
N-(*m*-Tolyl)-2-aminonaphthalene-6-sulfonate	25,200	2800		18,400	
N-(*p*-Tolyl)-2-aminonaphthalene-6-sulfonate	24,800	2900		18,700	
Naphthalene-2-sulfonate			20,700	19,500	18,300

fluorescence at 77°K is broad and structureless, whereas the phosphorescence is narrow and structured. This strongly suggests that the dipole moment of the triplet state, T_1, is considerably smaller than that of the first excited singlet state.

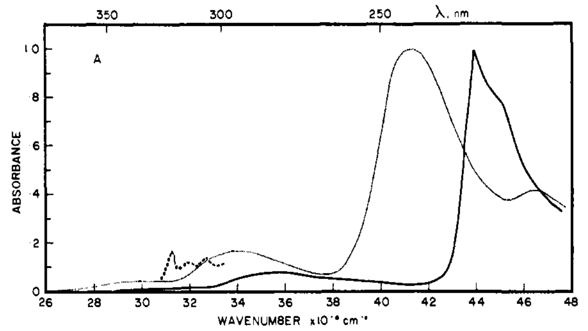

Figure 7. Absorption spectra of 2-aminonapthalene-6-sulfonate in aqueous solution at 300°K: ——, 3 *N* HCl; ...., pH 7; ----, an expansion of the solid line.

The Acid–Base Dependence of the Absorption and Fluorescence Spectra. It has been suggested that, for aromatic amines such as aniline, the two lowest energy absorptions in the singlet manifold have intramolecular charge-transfer character of the orbital promotion type $a_\pi \leftarrow 1$.[23] This electronic transition involves the promotion of a partially bonding "1" electron of the nitrogen atom to an antibonding orbital of the aromatic moiety of the molecule.

Since the addition of a proton to the amine group in the ground state of the molecule to form the ammonium ion involves the interaction of that proton with the 1 electrons, the $a_\pi \leftarrow 1$ transitions should shift to higher energies. Thus a thorough study of the absorption and fluorescence spectra was made during the protonation of the amine groups of the molecules studied here.

The variation of the absorption spectra of two of the molecules in this study, before and after the addition of proton to their amine groups, is shown in Figures 7 and 8. The spectra show that even for those molecules that have an aryl-substituted nitrogen atom, the absorption spectrum shows no indication of the aryl absorption at this resolution. This is reasonable since the extinction of the aryl portion alone would be expected to be more than an order of magnitude smaller than that of naphthalene-2-sulfonate over the region of the spectrum shown here.

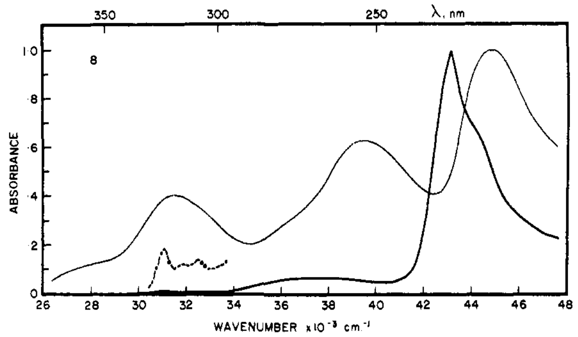

Figure 8. Absorption spectra of *N*-phenyl-*N*-methyl-2-aminonaphthalene-6-sulfonate in aqueous solution at 300°K; ——, 6 *N* HCl; ...., pH 7; ----, an expansion of the solid line.

For all the molecules in this study, protonation of the amine groups in the ground states of the molecules resulted in the loss of at least the two lowest energy transitions and the appearance of a spectrum virtually identical with that of naphthalene-2-sulfonate. The results suggest that the two lowest energy transitions of all these molecules are similarly derived from the parent hydrocarbon naphthalene. However, the bands to higher energies of the first two are derived in a very complex way. It is thus not clear that the third and fourth bands of 2-aminonaphthalene-6-sulfonate correspond to those observed in the remainder of the molecules.

Excited-state ionization of an amine proton during the lifetime of the first excited singlet state has been proposed to account for the fluorescence properties of aminonaphthalenesulfonates.[24] The p*K* values for the protonation of the amine groups in the ground states of 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate are known. These two molecules were investigated first, because at least one p*K* was known for each molecule, second, because the primary amine group might provide a basis for understanding the derived amines, and, third, because the role of the sulfonate group might be more easily understood from a study of two primary amines.

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[23] M. Kasha and H. R. Rawls, *Photochem. Photobiol.*, 7, 561 (1968).

[24] L. Stryer, *J. Amer. Chem. Soc.*, **88**, 5708 (1966).

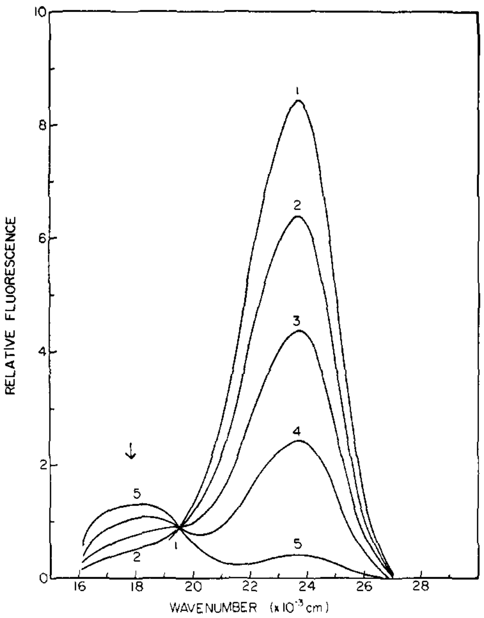


Figure 9. Fluorescence spectra of 2-aminonaphthalene-6-sulfonate during an alkaline titration: 1, pH 6.9; 2, pH 11.4; 3, pH 11.8; 4, pH 12.15; 5, pH ~12.4. The arrow denotes the emission maximum of the lower energy fluorescence.

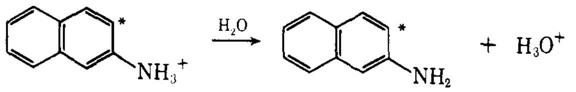
Determination of the p*K* values of the amine groups of these two molecules was done by titration with either acid or base and then measurement of both the spectrum and pH. Experimental values thus obtained were analyzed by computing the p*K* that gave the best least-squares deviation (±0.01 pH unit) from the experimental points.

Typical results for 2-aminonaphthalene-6-sulfonate during a titration of the amine in the ground state of the molecule showed isobestic points at 43.29×10^3, 38.31×10^3, and $36.36 \times 10^3\ \mathrm{cm}^{-1}$. The p*K* for this process was found to be 3.72, which was in excellent agreement with the value of 3.74 obtained by Bryson.[25] A similar titration for 2-aminonaphthalene showed isosbestic points at 38.31×10^3, 38.17×10^3, and $36.50 \times 10^3\ \mathrm{cm}^{-1}$. The p*K* value for this molecule was found to be 4.08, which was in excellent agreement with 4.11 found by Bryson.[25]

The further addition of acid to an aqueous solution of the protonated form of either 2-aminonaphthalene or its sulfonate analog resulted in no changes in their absorption spectra.

The addition of strong base to an aqueous solution of these molecules at neutral pH did not produce any changes in their absorption spectra. Even in 1 *N* KOH, the absorption spectra are identical with those at neutral pH. If ionization of an amine proton occurred in the solutions studied here, a significant change in the absorption spectrum would have been expected. Thus, it can be concluded that no ionization of an amine proton in the ground states of 2-aminonaphthalene or 2-aminonaphthalene-6-sulfonate occurred in alkaline solution. Experiments analogous to those described above were done with naphthalene-2-sulfonate; no changes were found for this molecule. The effects observed with the two amine derivatives may be attributed to the amine group alone.

Determination of the *ground-state* p*K* values for the protonation of the amine groups of these two molecules by fluorescence while exciting at the lowest energy absorption band of the unprotonated compound and monitoring the fluorescence of the unprotonated molecule resulted in the same value, within the limits of experimental accuracy, as that obtained from the absorption measurement. Note that a titration done in this manner does not give the correct *ground-state* p*K* value unless the reaction



is complete as written with respect to *both* rate and equilibrium in the excited state over the range of pH in question.

Since the absorption spectra of 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate show large changes during protonation of their amine groups in their ground states, excitation of their fluorescence was done at one of the isosbestic points in order to easily detect any changes in their fluorescence quantum yields *during* protonation in the ground state. When these experiments were done, no changes in the fluorescence quantum yields of the nonprotonated forms were found. Since the fluorescence of the protonated species would be expected to be different from that of the nonprotonated molecules, the lack of a pH dependence of the quantum yield over the pH region where the amine is being protonated in the ground state strongly suggests that the loss of a proton during the lifetime of the first excited singlet state was complete. Thus it is reasonable to assume that for 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate an *equilibrium* can be attained for proton-transfer processes during the lifetime of the first excited singlet state.

The addition of acid beyond that necessary to completely titrate the amine in the ground state of either of these two molecules, resulted in a decrease in the fluorescence quantum yield of the nonprotonated species. Furthermore, as the quantum yield decreased a new higher energy fluorescence appeared. This new emission was nearly identical in fine structure and energy with that of naphthalene-2-sulfonate under the same conditions. A similar titration with naphthalene-2-sulfonate showed that no changes occurred with this molecule. This pH-dependent quenching process was reversible and occurred for both 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate. The quenching of the lower energy fluorescence bands was quantitated as before and p*K* values calculated. The p*K* for 2-aminonaphthalene was 0.64; that for 2-aminonaphthalene-6-sulfonate was −0.02. This phenomenon may be attributed to protonation of the amine group during the lifetime of the first excited singlet state.

Although the data presented above strongly suggest that equilibrium is attained during the first excited singlet state, it is not altogether certain that this is the case. Therefore these excited state p*K* values and those presented later in this paper may not be the true equilibrium values. However, they are at least very close to the equilibrium values.

It is expected that the sulfonate group would be protonated with a p*K* ~ 0. However, no effects at-

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(25) A. Bryson, *Trans. Faraday Soc.*, 47, 522 (1951).

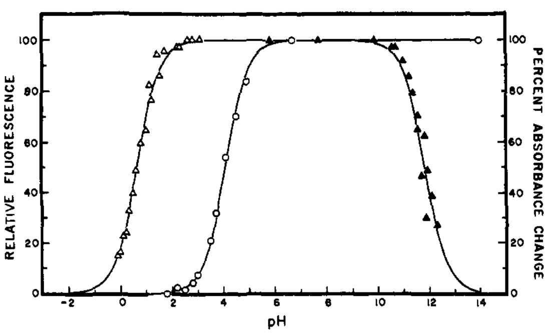


Figure 10. Titration curves of 2-aminonaphthalene: O, per cent absorbance change of the lowest band as a function of pH; Δ, fluorescence titrations in the acid region obtained by exciting the fluorescence at an isosbestic point in the absorption spectra; ▲, fluorescence titrations in the alkaline region; ——, computed titration curves.

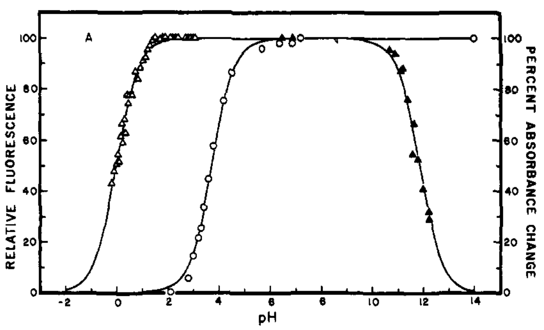


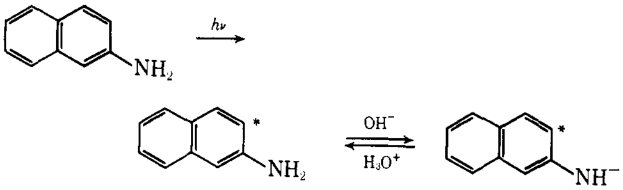
Figure 11. Titration curves of 2-aminonaphthalene-6-sulfonate: O, per cent absorbance change of the lowest energy band as a function of pH; ▲, fluorescence titrations in the acid region obtained by exciting the fluorescence at an isosbestic point in the absorption spectra; ▲, fluorescence titrations in the alkaline region; ——, computed titration curves.

tributable to this process were observed. On the other hand, the sulfonate group, protonated or not, shows an influence on the p*K* values for the protonation of the amine group in both the first excited singlet and ground states. In both electronic states the sulfonate moiety increases the acidity of the amine group over that of 2-aminonaphthalene.

The fact that the emissions of the protonated forms of the two molecules studied above are very similar in shape and energy to that of naphthalene or naphthalene-2-sulfonate indicates that the inductive effect of the ammonium group on the first excited singlets of these molecules is small. It is known that the inductive effect of this group is also small in the ground singlet state, and the measurements here are in agreement with that observation.[26]

When an aqueous solution of 2-aminonaphthalene or 2-aminonaphthalene-6-sulfonate is made sufficiently alkaline (pH >9), a new lower energy fluorescence appears while the original fluorescence decreases. There are no changes in the absorption spectra of these two molecules under these conditions. The appearance of this new fluorescence was reversible, and a similar experiment with naphthalene-2-sulfonate showed that no significant changes in its quantum yield of fluorescence occurred. The appearance of this new emission is shown in Figure 9 for 2-aminonaphthalene-6-sulfonate. An isoemissive point was found at 19.57×10^3 cm^{-1}. Analysis of the *disappearance* of the fluorescence band observed at neutral pH values assuming a simple equilibrium process gave a p*K* of 11.86. When the analogous experiment was done with 2-aminonaphthalene, an isoemissive point was found at 19.84×10^3 cm^{-1} and a p*K* calculated to be 11.86. In order to avoid the interference of external quenching effects, the p*K* values were also computed by quantitating the *appearance* of the new lower energy emission. These p*K* values were identical (within the experimental error of 0.05 pH unit) with those previously calculated. For example, the value of 2-aminonaphthalene-6-sulfonate by the second method was 11.87.

Although the origin of the new emission is not altogether certain, its appearance probably corresponds to the formation of the naphthylamide (sulfonate) ion during the lifetime of the first excited singlet state. The following equation illustrates this process.



Similar behavior has been reported for aminopyrenesulfonates.[27] It is not certain that the naphthylamide (sulfonate) ion is the luminescent molecule. An intermolecular charge-transfer species in which an electron is at least partially transferred to another molecule in solution, be it solvent or otherwise, has not been ruled out in this case. However, previously published luminescence spectra of simple salts of the naphthylamide ion in aprotic solvents[28] strongly suggest that the emitting molecule is the naphthylamide (sulfonate) ion itself.

The acid-base properties of 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate are summarized by the curves shown in Figures 10 and 11. The open circles denote the processes in their ground states. The open triangles denote the protonations of the amine groups to form the positive ammonium group during the lifetime of the first excited singlet state. The solid triangles represent the deprotonation of the uncharged amine groups in the excited state to form their corresponding naphthylamide (sulfonate) ions. The curves that are drawn were computed from the p*K* values obtained by least squares.

The acid-base behaviors of these two molecules are qualitatively similar. The influence of the sulfonate group on the formation of the naphthylammonium ion in either the ground state or first excited singlet was clear. The sulfonate group added to the 6 position of 2-aminonaphthalene lowered the p*K* values, or increased the acidity in both electronic states. The magnitude of this effect was slightly larger for the first excited singlet state than for the ground singlet state. This fact suggests that the amount of intramolecular charge transfer is greater in the first excited singlet than in the ground state. The sulfonate group showed no influence on the p*K* value of deprotonation of the uncharged amine group to form the naphthylamide (sulfonate) ion.

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[26] D. M. Bishop and D. P. Craig, *Mol. Phys.*, **6**, 139 (1963).

[27] Th. Forster, *Z. Elecktrochem.*, **54**, 42 (1950).

[28] E. Doller, Th. Forster, and H. Renner, *Z. Phys. Chem.* (*Frankfurt am Main*), **15**, 34 (1958).

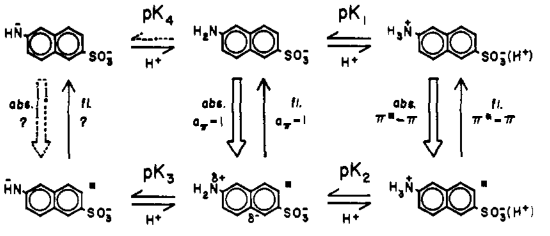

Figure 12. The ground- and excited-singlet-state reactions of 2-aminonaphthalene-6-sulfonate in aqueous solution with varying pH.

Several important conclusions can be made from the spectroscopic properties of 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate that have been presented above. (1) The inductive effect of the ammonium group at the 2 position of naphthalene or naphthalene-2-sulfonate is small for both the first excited and ground singlet states. (2) Excited-state ionization of an ammonium group proton of the naphthylammonium (sulfonate) ion during the titration of the amine group in the *ground state* is complete. (3) The sulfonate group affects the formation of the naphthylammonium (sulfonate) ion in the same manner in both the first excited and ground singlet states. On the other hand, the sulfonate group has no measureable effect on the p*K* for the formation of the naphthylamide ion in the excited state. (4) The role of the sulfonate group is to increase the amount of intramolecular charge transfer in both the ground and first excited singlet states. Furthermore, the intramolecular charge-transfer transition is of the $a_\pi \leftarrow l$ type described by Kasha.[23]

Figure 12 describes the acid–base behavior of 2-aminonaphthalene-6-sulfonate on a molecular basis. An analogous diagram could be constructed for 2-aminonaphthalene. The experimental p*K* values obtained for both of these molecules are given in Table IV along with literature values where known. It will be noted that there is a large discrepancy between the value for pK_2 of 2-aminonaphthalene given by Jackson and Porter[29] and that obtained in this study. Calculation of the excited-state p*K* values for 2-aminonaphthalene and 2-aminonaphthalene-6-sulfonate from the equilibrium thermodynamic relationship given by Weller[30]

$$pK^* = pK - \frac{0.625}{T}\Delta\bar{\nu}_h$$

resulted in values which were in excellent agreement with those reported here.

Table IV. Listing of p*K* Values of 2-Aminonaphthalene and 2-Aminonaphthalene-6-sulfonate

Molecule	p*K*	Exptl ± 0.05 unit	Calcd p*K* value	Lit.
2-Aminonaphthalene	pK_1	4.08		4.11[a]
	pK_2	0.64	0.6	−2[b]
	pK_3	11.86		
	pK_4	14		
2-Aminonaphthalene-6-sulfonate	pK_1	3.72		3.74[a]
	pK_2	−0.02	0.0	
	pK_3	11.86		
	pK_4	14		

[a] Reference 25. [b] Reference 29.

As is indicated in the diagram, the electronic transition between the ground and first excited singlet states at neutral pH or above corresponds to a partial transfer of an l electron of the nitrogen atom to an antibonding π orbital of the naphthalene ring system. Once the molecule has been promoted to its first excited singlet state, its amine groups may either eject a proton to form the naphthylamide (sulfonate) ion or it may remain unchanged. Thus, the fluorescence at pH values greater than or equal to neutrality will reflect the proportion of each of these two molecular species. If the pH of the medium is greater than that for the onset of excited state protonation, but less than that necessary to form the naphthylammonium (sulfonate) ion in the ground state, for example, $1 \leq \mathrm{pH} \leq 3.72$ for 2-aminonaphthalene-6-sulfonate, the fluorescence will originate solely from the 2-aminonaphthalene (sulfonate) molecule. However, the excited state arose from a ground-state population of molecules whose predominant species was the *naphthylammonium* (sulfonate) molecule. If the pH of the medium is low enough, for example, $\mathrm{pH} \leq -0.02$ for 2-aminonaphthalene-6-sulfonate, the predominant fluorescent species will be the excited *naphthylammonium* (sulfonate) molecule. The equilibrium designated by pK_4 has not been observed in aqueous media.

As was previously demonstrated, those molecules having alkyl- or aryl-substituted nitrogen atoms could also be reversibly protonated in their ground states to form their corresponding naphthylammonium ions. However, secondary and tertiary amines exhibit ground-state p*K* values for this process which are much lower than those for the two primary amines already studied. In addition, the quenching of fluorescence by high concentrations of hydronium ions alone becomes significant below pH ~0. The p*K* values for the excited-state processes of the nitrogen-substituted compounds are below pH 0. Thus, the same type of approach used to study the two primary amines above could not be applied to the remainder of the molecules in this study.

However, since substitution of electron donating groups, such as phenyl, on the nitrogen atom of 2-aminonaphthalene-6-sulfonate might in some way result in the lowering of the p*K* for excited-state formation of the naphthylamide ion (*cf.* pK_3 in Figure 12), an investigation of the fluorescence of several *N*-arylaminonaphthalenesulfonates was made in alkaline media. It has previously been shown[31] for other position isomers of one of the molecules in this study that excited-state ionization did not occur for $0 \leq \mathrm{pH} \leq 14$. Titrations over the pH range $0 \leq \mathrm{pH} \leq 13$ for the *N*-arylaminonaphthalenesulfonates studied here confirmed that finding.

It is important to reemphasize that the ground-state formation of the ammonium ions of the nitrogen-substituted molecules was exactly analogous to the behavior of the primary amine derivatives. There is no reason not to expect the substituted-amine molecules to behave analogously in the first excited singlet states.

As further evidence that protonation or deprotonation is not involved in the excited-state processes of these molecules, a pH study of *N*-phenyl-*N*-methy-2-aminonaphthalene-6-sulfonate was made. This molecule has

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

(30) A. Weller, *Progr. React. Kinet.*, **1**, 189 (1961).

(31) D. C. Turner and L. Brand, *Biochemistry*, 7, 3381 (1968).

no ionizable proton. The luminescence behavior of this molecule in aqueous media was essentially the same as that of its nonmethylated analog, *N*-phenyl-2-aminonaphthalene-6-sulfonate. These studies show beyond any doubt that the formation of the naphthylamide ion in the first excited singlet states of *N*-arylaminonaphthalenesulfonates does not occur in aqueous solution for $0 \leq \mathrm{pH} \leq 13$. Furthermore, the luminescence properties of *N*-arylaminonaphthalenesulfonates are not determined by the presence of an amine proton.

In summary, excited-state ionization of an amine proton in aqueous solution at neutral pH is not involved in the excited-state processes of any of the molecules in this study including the primary amine derivatives.

The energies of the absorption and emission bands and the shapes of the spectra of all these molecules when their amine groups are protonated show that at least the two lowest energy absorptions in the singlet manifolds have significant intramolecular charge-transfer character. The electron-withdrawing power of the sulfonate group is well known.[25] Thus the addition of the sulfonate group in the 6 position of 2-aminonaphthalene would be expected to result in a lowering of the energies of the two lowest energy transitions. These effects are clearly found for 2-aminonaphthalene and also for *N*-phenyl-2-aminonaphthalene (*cf.* Table I). It will be recalled that the second absorption band in 2-aminonaphthalene is found as a shoulder on the band found at $34–38 \times 10^3\ \mathrm{cm}^{-1}$.

The general results of the composite molecule approach should be applicable to the molecules considered here. Namely, the energies of those bands corresponding to charge-transfer transitions will be proportional to the difference in the ionization potential of the electron donator portion and the electron affinity of the electron acceptor portion of the molecule *less* the Coulomb interaction integral between the resultant positive and negative charge distributions. It should be pointed out that in the case of *N*-aryl-2-aminonaphthalenes the local excited states of the aryl group may become significant. In addition, it is known that for aromatic amines such as aniline, the overlap integrals of the type $\langle l_N|\phi_C(2p\pi)\rangle$ between the nitrogen l electron orbital and the adjacent carbon $2p\pi$ orbital when reduced to atomic orbital terms vary as $\cos\theta$, where θ is the angle of twist.[23] The state energies have also been found to vary with θ for aniline.[10–12] Thus, substitution of the nitrogen atom of 2-aminonaphthalene or 2-aminonaphthalene-6-sulfonate with chemical groups of varying sizes and geometries might result in spectral shifts in the two lowest energy absorption bands which do not strictly fall in the order predicted by the composite molecule approximation. However, the general trend in the energies of the two lowest transitions when considering a large number of derivatives should be that the energies decrease as the ionization potentials of the amine groups decrease and/or the electron affinities of the naphthalene rings increase. For anilines it has been shown that the oscillator strengths increase as the ionization potential of the amine group decreases.[14] Although exceptions to the rule occur (*cf.* Table I), it generally holds that the energies of the lowest energy absorption bands decrease as the ionization potentials of the amine groups decrease and/or the electron affinities of the naphthalene rings increase. It also generally holds that the oscillator strength of the lowest energy absorption increases in roughly the same order. More frequent exceptions were found for the second absorption band, but the general behavior was essentially the same as for the lowest energy band.

As a further examination of the behavior of the energies of the two lowest energy absorptions, a study of the absorption spectrum of *N*-(*p*-hydroxyphenyl)-2-aminonaphthalene was made under various conditions. By virtue of its phenolic group this molecule has an electron-donating group whose ionization potential may be decreased by titration of the phenolic proton. The ionization potential of the phenolate anion would be lower than that of the phenolic group. Several experiments in different solvent systems were performed. Among the solvents used were 90% ethanol–10% water (v/v), absolute ethanol, and *tert*-butyl alcohol. In each case titration of the phenolic proton resulted in a small lowering of the energies of the first two absorption bands. The largest changes occurred when a hydrogen-bonding solvent such as ethanol or methanol was added to a cyclohexane solution of this molecule.

It has been common to consider the effects of substituent groups on molecules such as naphthalene as small perturbations on the lower lying electronic states of the parent hydrocarbon.[6] This approach has met with considerable success for such weakly interacting groups as methyl, ethyl, etc. However, in the case of the amine group, the unshared pair of electrons is known to constitute strong interaction with the π-electron system of the parent hydrocarbon. Therefore, considering the final electronic states of the molecules in this study as *perturbed* $^1B_{3u}{}^-$ and $^1B_{2u}{}^+$ states of naphthalene is of questionable validity. When the sulfonate group is attached to the 6 position of the naphthalene ring, the perturbation approach would become even more questionable. Therefore, when speaking of the two lowest energy transitions of the aminonaphthalenesulfonates, they have been referred to as intramolecular charge-transfer bands to emphasize that they contain a certain percentage of charge-transfer character. This is not to say that these bands are *predominantly* intramolecular charge-transfer bands, but it is to say that it is this property that seems to be responsible for the luminescence behavior observed. The systematic behavior of the luminescence from molecule to molecule in the series of compounds studied here bears this out.

While the higher excited singlet levels have not been specifically studied here, a comment or two can be made about them. First, it is not altogether clear that these bands contain significant charge-transfer character. Second, the absorption spectra of *N*,*N*-dimethyl-2-aminonaphthalene-6-sulfonate and *N*-cyclohexyl-2-aminonaphthalene-6-sulfonate have similar bands centered at 40×10^3 and $46 \times 10^3\ \mathrm{cm}^{-1}$. The bands at the lower energy are more intense relative to the others. It is tempting to assign the lower energy bands to the ones found common to all the aryl-substituted derivatives centered at about $38 \times 10^3\ \mathrm{cm}^{-1}$. Whether or not this lower energy band is derived from the forbidden $^1B_{1g}{}^+$ transition in naphthalene[32] is a matter of speculation at this point.

As a final topic in the discussion of the characteristics of the electronic states of the molecules in this study, the

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(32) H. Baba and S. Suzuki, *Bull. Chem. Soc. Jap.*, **34**, 82 (1961).

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 $CT(S_1) > CT(T_1) \geq CT(S_0)$. (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.

Acknowledgments. The authors thank Professors M. Kasha, E. White, and R. Biltonen for helpful discussions.

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[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

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[1] Contribution No. 645 from the McCollum–Pratt Institute. This research was supported by NIH Grant No. G.M. 11632. A preliminary account of this work has appeared in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969.

[2] Based in part on a thesis submitted by C. J. S. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The Johns Hopkins University.

[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).