(15) M. Tanaka, S. Kaneshina, K. Shin-No, T. Okajima, and T. Tomida, *J. Colloid Interface Sci.*, **46**, 132 (1974).
(16) S. Kaneshina, M. Tanaka, T. Tomida, and R. Matuura, *J. Colloid Interface Sci.*, **48**, 450 (1974).
(17) M. Tanaka, S. Kaneshina, S. Kuramoto, and R. Matuura, *Bull. Chem. Soc. Jpn.*, **48**, 432 (1975).
(18) S. D. Hamann, "Modern Aspects of Electrochemistry No. 9", B. E. Conway and J. O'M. Bockris, Ed., Plenum Press, New York, N.Y., 1974, p 47.
(19) K. Suzuki and Y. Taniguchi, "The Effects of Pressure on Organisms", Symposia of the Society for Experimental Biology XXVI, Academic Press, New York, N.Y., 1972, p 103.
(20) D. B. Fitchen, *Rev. Sci. Instrum.*, **34**, 673 (1963).
(21) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **66**, 185 (1931).
(22) J. E. Gordon and R. L. Thorne, *J. Phys. Chem.*, **71**, 4390 (1967).
(23) R. L. Bohon and W. F. Claussen, *J. Am. Chem. Soc.*, **73**, 1571 (1951).
(24) K. Suzuki, Y. Taniguchi, T. Ishigami, and M. Tsuchiya, "Proceedings of the 4th International Conference on High Pressure", Physical Chemists Society of Japan, Kyoto, 1974, p 615.
(25) K. Shinoda, Ed., "Solvent Properties of Surfactant Solutions", Marcel Dekker, New York, N.Y., 1967.
(26) P. Mukerjee and K. J. Mysels, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 36** (1971).
(27) S. J. Rehfeld, *J. Phys. Chem.*, **74**, 117 (1970).
(28) W. K. Mathews, J. W. Larsen, and M. J. Pikal, *Tetrahedron Lett.*, **6**, 513 (1972).

Intramolecular Donor–Acceptor Systems. 2. Substituent Effects on the Fluorescence Probes: 6-(*N*-Arylamino)-2-naphthalenesulfonamides

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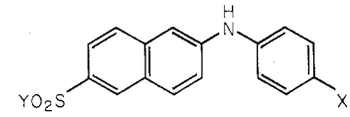
The fluorescent probes, 6-(*N*-arylamino)-2-naphthalenesulfonamides (**1a–c**, **2a–c**), all exhibit charge-transfer fluorescence behavior consistent with the general scheme previously proposed. No special solvent effects are required to explain the data for the corresponding sulfonates.

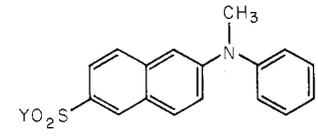
Fluorescent molecules which are added to various systems for the purpose of revealing characteristics of the system to which they are added are called probes. In general, some fluorescence parameter of the probe molecule is altered within the system. Among the parameters which might be examined are emission maximum, fluorescence lifetime, and excitation spectrum. In order to interpret changes in the parameter used, a precise understanding of the origin of the fluorescence emission is necessary. In cases for which only the presence or absence of the probe is evaluated (localization within cells or within cell organelles, motion of labeled system, etc.), knowledge about the mechanism is still important so that quenching or promoting conditions will not cause the results to be misinterpreted.

Among the fluorescent probes which have been often used for biochemical and biological systems (see the review by Azzi[2]) are 6-(*N*-arylamino)-2-naphthalenesulfonates (ANS, e.g., **2a**). The key to understanding the fluorescence of ANS lay in use of solvent polarity parameters (such as, $E_T(30)$ and Z values[3]) which revealed the existence of two rather different fluorescence emissions from a number of ANS derivatives.[4] An earlier and somewhat similar study by Turner and Brand[5] combined data from so many different solvents that the change in emission type was obscured. Many further investigations on ANS derivatives using solvent polarity effects, solvent viscosity effects, fluorescence lifetimes, and excited state spectra (using laser pulse excitation) have led to considerable clarification in the radiative and nonradiative processes which ensue after light absorption by ANS derivatives.[6] ANS derivatives may be viewed as intramolecular donor–acceptor systems in which, for all cases of interest in this article, the *N*-phenyl group is a donor and the naphthalenesulfonate moiety is an acceptor. The appearance of two emissions can be explained in terms of two excited states, $S_{1,np}$ (phenyl group perpendicular to the naphthalene ring) and $S_{1,ct}$ (phenyl group radical cation perpendicular to a naphthalene radical anion) which respond differently to intramolecular changes (substituent polarity and size, heavy atom effects)[7] and extramolecular changes (solvent polarity and viscosity). A slightly condensed version of the scheme for ANS derivatives is shown in Figure 1.

Greene[8] has recently reported the interesting result that conversion of the sulfonate group of the usual ANS derivative to a sulfonamide (i.e., **2a** → **2b** or **2c**) led to compounds for which the emission maxima were "much more sensitive to solvent polarity" than those of the sulfonate. It was suggested that the sulfonate was anomalous in response due to some unspecified combination of general and specific solvent polarity effects. In order to find out if the sulfonamide emissions fit the scheme shown in Figure 1, we have reexamined the compounds of Greene together with a number of new ANS derivatives. Our results show quite clearly that the sulfonamide fluorescences are charge transfer (emissions from an $S_{1,ct}$ state) and are completely consistent with our general scheme for ANS excited state processes.



1a: Y = $N(CH_3)_2$, X = H
b: Y = $N(CH_3)_2$, X = CH_3
c: Y = $N(CH_3)_2$, X = OCH_3
2a: Y = O^-Na^+, X = CH_3
b: Y = NH_2, X = CH_3
c: Y = $NHCH_2CH_2{}^+NH_3$, Cl^-, X = CH_3



3a: Y = $N(CH_3)_2$
b: Y = Cl

Experimental Section

Syntheses of ANS derivatives (**1a–c**, **3a,b**) were carried

TABLE I: Emission Data for 1a,b and 2b,c in Dioxane-Water Mixtures[a,b]

Solvent % dioxane-water[c]	$E_T(30)$ value[d]	$\lambda_{max}(\Phi_F)$[f] 1a	1b	2b	2c
100	36.1	420(0.57)	438(0.50)	433(0.60)	438(0.40)
99.60	37.1	423(0.62)	440(0.50)	436(0.58)	441(0.35)
99.0	38.6	426(0.66)	443(0.45)	440(0.60)	445(0.38)
98.1	41.2	429(0.66)	450(0.44)	445(0.64)	450(0.34)
96.1	42.9	434(0.57)	458(0.36)	451(0.51)	460(0.27)
95.2	43.5	437(0.56)	465(0.33)	456(0.43)	466(0.24)
94.2	44.4	440(0.55)	470(0.27)	461(0.42)	471(0.20)
92.3	45.7	444(0.49)	474(0.18)	466(0.33)	476(0.14)
90.3	46.6	450(0.39)	479(0.10)	471(0.15)	480(0.10)
85.5	47.9	455(0.34)	485(0.09)	476(0.11)	485(0.05)
80.6	48.9	460(0.27)	490(0.08)	480(0.09)	490(0.03)
75.8	49.8	465(0.19)	g	485(0.05)	494(0.02)
71.0	50.7	469(0.14)		488(0.04)	g
66.1	51.5	473(0.10)		491(0.03)	
61.3	52.1	476(0.07)		494(0.02)	
56.5	52.8	480(0.07)		g	
51.0	53.4	g			

[a] Temperature 25 ± 2 °C. Temperature effects on the position of the fluorescence maximum or the intensity of the emission over this temperature range are small. [b] For details of the measurements and instrumentation refer to the Experimental Section. [c] Percentage of dioxane by volume mixed with water. [d] Values were either taken from Table 2, p 28 in Ch. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, 11, 1 (1968) or derived from values in that table by linear interpolation. [e] In nanometers ± 10% or less, according to reproducibility. Quinine sulfate in 0.1 N H_2SO_4, Φ_F = 0.55. [g] Solutions of this polarity or greater exhibited the fluorescence of a protonated form (Dodiuk and Kosower, ref 19).

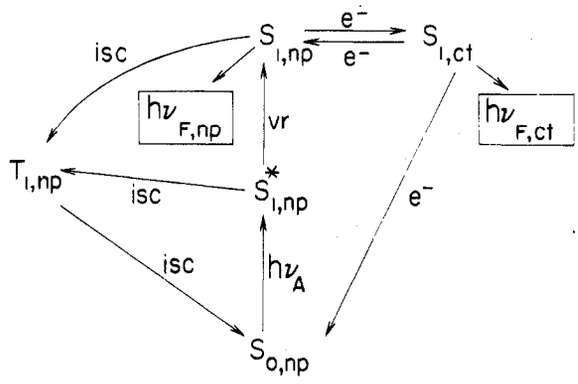


Figure 1. A scheme illustrating some of the excited states which participate in the radiative and nonradiative processes which follow absorption of light by a 6-(*N*-arylamino)-2-naphthalenesulfonate. The symbols are as follows: $S_{0,np}$, ground state with nonplanar (np) relationship between the planes of the *N*-aryl group and the naphthalene ring; $S_{1,np}$*, vibrationally excited lowest excited singlet state; $S_{1,np}$, relaxed lowest excited singlet state; $S_{1,ct}$, charge-transfer state, in which an electron has been transferred from the aryl group to the naphthalene ring (the nitrogen p orbitals are conjugated with the phenyl radical cation); $T_{1,np}$, triplet state; isc, intersystem crossing; vr, vibrational relaxation; e^-, electron-transfer process; $h\nu_F$, fluorescence emission; $h\nu_A$, light absorption. (For a more complete version of the scheme, see Kosower et al.[6,19])

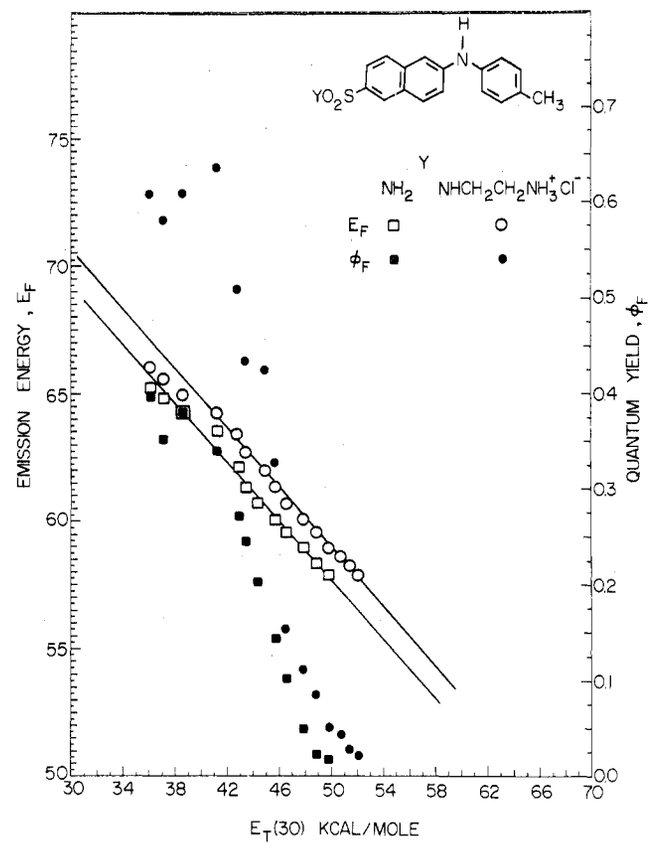


Figure 2. A plot of emission energies, E_F, and emission quantum yields for **2b** and **2c** vs. the solvent polarity parameter, $E_T(30)$, using fluorescence maxima obtained for a series of dioxane–water solutions. All units are in kilocalories per mole.

out according to Greene[8] by a modification of the method of Cory et al.,[10] using 40% aqueous dimethylamine as the amine. Chromatography on silica gel and/or crystallization were used to obtain pure products (single spot on TLC with CH_3OH:benzene 40:60) for which NMR and UV were used to establish structures.

1a: mp 115–116 °C; NMR, $CDCl_3$ arom H, δ 7–8.3, m; NH δ 6.1–6.2, 1 H, broad s, removed with D_2O; $N(CH_3)_2$, δ 2.75, s, 6 H; UV, 278 (29 000), 329 (26 300), 359 (7300)[18] maxima in dioxane.

1b: mp 136–137 °C, crystallized from Me_2CO–H_2O; NMR, **1a** + CH_3, δ 2.34, 3 H, s; UV, 278 (22 600), 329 (20 700), 360 (7300)[18] maxima in dioxane.

1c: mp 125–127 °C; NMR, **1a** + CH_3O, δ 3.8, 3 H, s; UV 269 (26 700), 324 (22 300), 362 (6700)[18] in dioxane.

3a: mp 117–118 °C, crystallized from hexane–EtOAc; H NMR, **1a** + N–CH_3, δ 3.45, 3 H, s; UV identical with that of the amide (Cory et al.[10]).

3b: sulfonyl chloride was chromatographed on silical gel in CCl_4. UV as reported by Cory et al.[10] Structure of the water-sensitive compound confirmed by conversion to **3a**.

Absorption spectra were recorded on a Cary 17 spectrophotometer. Emission spectra were recorded on a

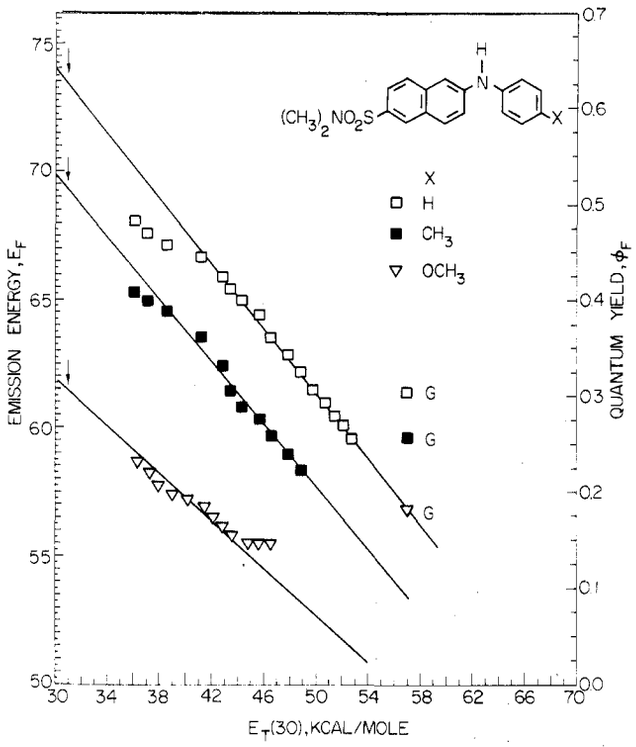


Figure 3. A plot of emission energies, E_F, for **1a**, **1b**, and **1c** vs. the solvent polarity parameter, $E_T(30)$, using fluorescence maxima obtained for a series of dioxane–water solutions. The emission energy for each substance in glycerol solution (point marked G) is also shown. All units are in kilocalories per mole. Arrows indicate values of extrapolated charge-transfer emission energy.

Perkin-Elmer-Hitachi Model MPF-4 spectrofluorimeter with corrected spectra attachment and a digital integrator was used, with quinine sulfate in 0.1 N H_2SO_4 as reference (ϕ_F = 0.55). Preparations of solutions and plotting of data were carried out as previously described (Kosower et al.).[6] Solutions of **1a–c** in glycerol contained 0.01% ethanol.

Results

Emission data, both maximum and quantum yield, were obtained in a series of dioxane–water solutions for the amides obtained from Greene[8] (**2b,c**). These data are listed in Table I and are plotted against the solvent polarity parameter $E_T(30)$ in Figure 2. It is worth reiterating that an intramolecular transition which involves considerable loss of charge separation is best compared to an *intra*molecular reference. Z values represent an *inter*molecular charge-transfer transition. In most solvents there is a proportionality between $E_T(30)$ and Z, the latter being appreciably more sensitive to solvent than the former. The use of solvent polarity parameters is discussed in depth by Kosower.[3]

The dimethylamide derivatives of 6-*N*-arylamino-2-naphthalenesulfonates were chosen as likely to be soluble in a suitable range of nonpolar solvents. Since they are easy to prepare, purify, and characterize, such derivatives might well be of interest in many cases. Data for three dimethylsulfonamides (**1a–c**) are also listed in Tables I and II, and are plotted against $E_T(30)$ in Figure 3.

The use of *N*-methyl ANS derivatives[9,10] as fluorescent probes in the form of amide derivatives[11,12] made a brief comparison of interest, and data for the dimethylamide **3a** are also given in Table III. The closely related chloride (**3b**) (of interest because of the strong electron-withdrawing power of the SO_2Cl group) could only be examined in CCl_4 (emission maximum 476 nm, $\phi_F = 4 \times 10^{-4}$) and was extremely sensitive to traces of water in most other solvents, yielding the sulfonate. Data for **3a** are plotted in Figure 4.

TABLE II: Emission Data for 1c in Dioxane-Water Mixtures[a]

Solvent % dioxane-water	$E_T(30)$ value	$\lambda_{max}(\Phi_F)$
99.9	36.3	487(0.10)
99.6	37.2	491(0.08)
99.3	37.9	495(0.07)
98.9	39.0	498(0.06)
98.0	41.4	502(0.05)
97.1	42.1	506(0.03)
96.1	42.8	509(0.02)
95.2	43.5	512(0.02)
93.6	44.8	515(0.01)
92.5	45.6	515(0.01)
90.5	46.5	515(0.01)
85.0	47.9	*b*

[a] See footnotes to Table I. [b] See footnote *g* of Table I.

TABLE III: Emission Data for 3a in Dioxane-Water Mixtures[a]

Solvent % dioxane-water	$E_T(30)$ value	$\lambda_{max}(\Phi_F)$
99.9	36.3	445(0.47)
99.6	37.0	450(0.45)
99.1	38.5	455(0.44)
98.1	41.4	460(0.44)
97.2	42.0	465(0.39)
95.3	43.2	470(0.37)
92.5	45.6	475(0.33)
90.6	46.5	480(0.30)
85.9	47.8	485(0.28)
81.3	48.7	494(0.19)
71.9	50.5	505(0.09)
62.5	52.0	510(0.06)
53.1	53.2	515(0.04)
43.2	54.9	520(0.02)
39.1	55.8	*b*

[a] See footnotes to Table I. [b] See footnote *g* of Table I.

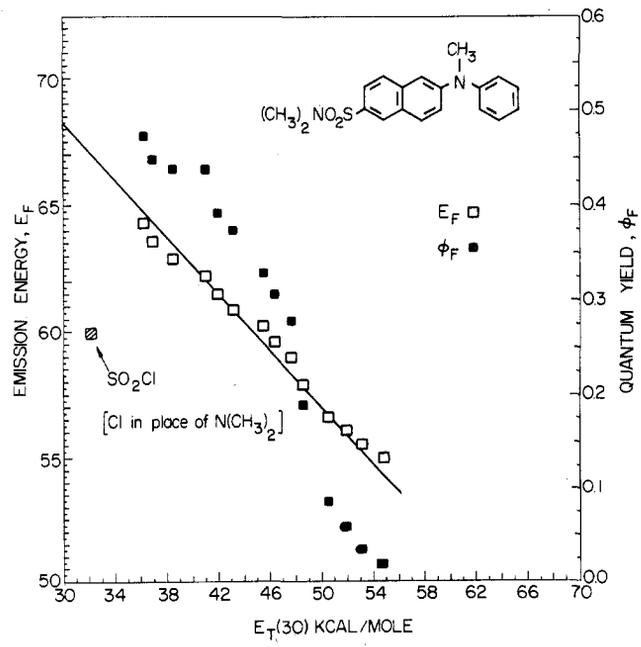


Figure 4. A plot of emission energies, E_F, and emission quantum yields for **3a** vs. the solvent polarity parameter, $E_T(30)$, using fluorescence maxima obtained for a series of dioxane–water solutions. The point for the sulfonyl chloride (**3b**, Y = Cl) in CCl_4 is also shown. All units are in kilocalories per mole.

TABLE IV: Emission Data for 1a-c in Glycerol

	λ_{max}, nm	ϕ_F [a]
1a	465	0.074
1b	480	0.056
1c	502	0.015

[a] Corrected for refractive index of glycerol.

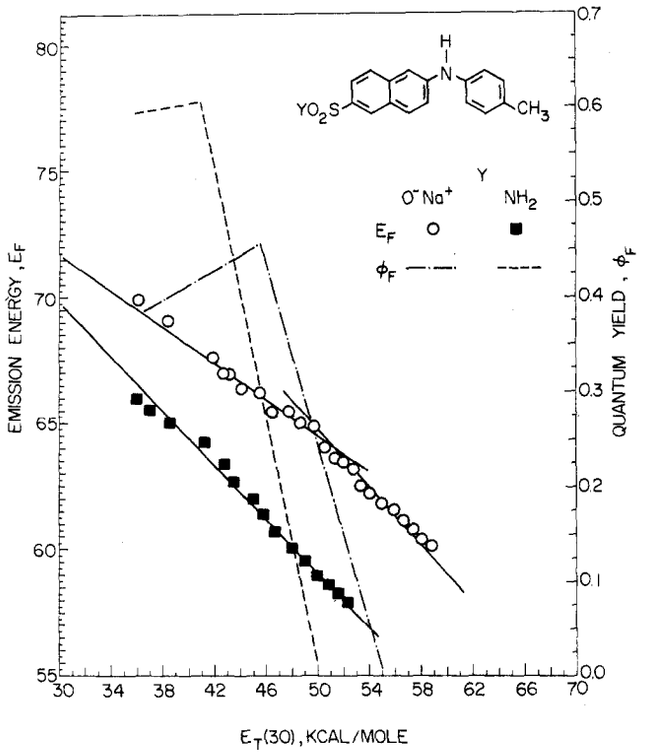


Figure 5. A plot of emission energies, E_F, and emission quantum yields for **2a** and the corresponding amide **2b** vs. the solvent polarity parameter, $E_T(30)$. Data for **2a** is taken from Kosower et al.[6] and that for **2b** from Figure 2. All units are in kilocalories per mole.

The dioxane-water results for all amide derivatives (**1a-c,2b,c**) may be summarized as follows. The emission energies uniformly yield almost parallel straight lines when plotted against $E_T(30)$, permitting extrapolation to hydrocarbon solvent ($E_T(30) = 31$) and allowing a reasonably accurate estimate of emission energies under nonsolvating conditions. The quantum yields of fluorescence for all derivatives fall off rapidly as solvent polarity is increased.

The points for the amides **1a,b** and **2b,c** in two or three of the least polar solvents fall somewhat below the correlation lines. The corresponding quantum yields show some deviation from a linear relation with solvent polarity, but do not rise as seen for **2a** in the same solvent polarity range.

Emission data for the amides **1a-c** in glycerol are listed in Table IV. The emissions are clearly different from those in dioxane-water solution.

Discussion

The effect on fluorescence emission which is produced by the change from a sulfonate to an amide group is best illustrated by a comparison plot for data on **2a** and **2b** (Figure 5). As previously demonstrated, the low slope region of the plot for the sulfonate represents emission from the $S_{1,np}$ state. The high slope portion of the plot correlates emissions from the $S_{1,ct}$ state. In particular, only a charge-transfer emission could exhibit so great a sensitivity to solvent polarity, with the slope of the plot against $E_T(30)$ being between 0.6 and 0.7. The fluorescence

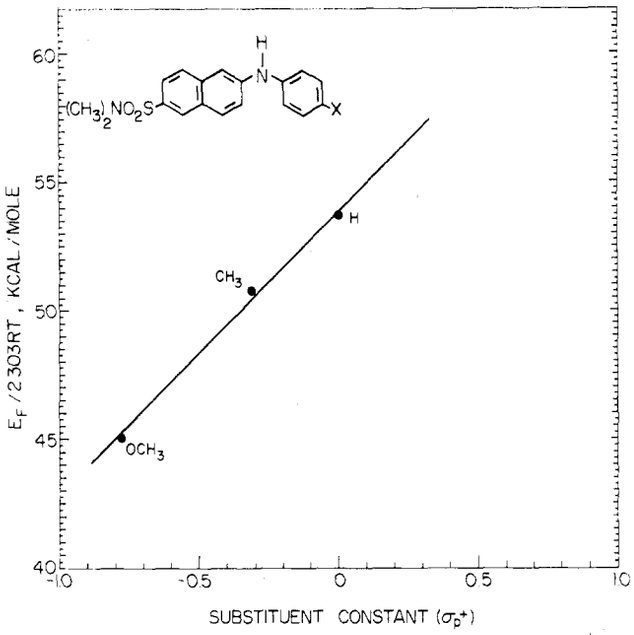


Figure 6. A plot of extrapolated emission energies (assigned as $S_{1,ct}$ emissions) divided by $2.3RT$ vs. the Hammett-Brown-Okamoto σ_p^+ parameter, using values for **1a-c**.

TABLE V: Extrapolated Values for $S_{1,ct}$ Emissions in Hydrocarbon Solvent[a,b] for ANS Derivatives

X = (in 1)	Y = $N(CH_3)_2$ $E_{F,ct}$, kcal/mol	σ_p^+	Y = O^- $E_{F,ct}$, kcal/mol	ΔE_F, kcal/mol
H(1a)	73.3	0	78.0	4.7
CH_3(1b)	69.3	−0.31	75.6	6.3
OCH_3(1c)	61.5	−0.78	69.2	7.7

[a] $E_T(30) = 31.0$. [b] See Figure 2 and Kosower et al.[6] for illustrations of the extrapolation lines.

quantum yield from the charge-transfer state ($S_{1,ct}$) is also very sensitive to solvent polarity, because the quenching reaction is an electron-transfer reaction.[6]

All of the amide derivatives (**1a-c, 2b,c**) exhibit emisions for which the energies and the quantum yields vary with solvent polarity in a way very much like that of the charge-transfer emission of the sulfonate. The slopes for the emission energy-solvent polarity correlations are between 0.6 and 0.7. We regard this similarity as strong evidence for the identification of the emitting states of the amides as $S_{1,ct}$.

The conclusions that the amide emitting states are charge transfer is confirmed through a correlation of the extrapolated emission energies with the Hammett-Brown-Okamoto substituent constant σ_p^+. The extrapolated emission energies are listed together with the substituent constants in Table II. The plot of the emission energies against substituent constants is shown in Figure 6. The slope, or ρ value, for the correlation is about −11, a value so high as to provide very clear evidence for the assignment of the emitting state as $S_{1,ct}$.

We may then ask why conversion of the sulfonate to sulfonamide has such a strong effect on the nature of the fluorescence emission observed. The answer is simply that the sulfonamide is a much stronger electron-withdrawing group than the sulfonate. The σ_p^- for the SO_2NH_2 group is 0.94 whereas for σ_p^- for SO_3^- group is 0.09 (we here assume that σ_p^- for $SO_3^- = \sigma_p$).[13] The extrapolated charge-transfer energies for the amides may be compared with the corresponding extrapolated values for $S_{1,ct}$

emissions for the sulfonates. The latter have been included in Table V and lead to an approximate ρ value for the naphthalene ring as an acceptor of 5.4, according to the relation, average $\Delta E_F/2.3RT = \rho(\Delta\sigma)$ in which $\Delta\sigma = \sigma_p^-(SO_2NH_2) - \sigma_p^-(SO_3^-)$. We would expect the ρ value for naphthalene charge-transfer processes to be much lower than that for benzene derivatives since the greater number of sites available for delocalizing charge diminishes the effect of the substituent. Thus, the change in the energy of the naphthalene–tropylium ion charge-transfer band for the substitution of a 2-methyl group is a little less than half of that for the substitution of a methyl group into benzene.[14]

In order to confirm that the scheme shown in Figure 1 applied in all of its details to the ANS amides, we also measured the emissions for **1a–c** in glycerol. Our previous work had shown that the high viscosity of glycerol lowered the rate for conversion of $S_{1,np}$ to $S_{1,ct}$, extending the lifetime of the $S_{1,np}$ state in the highly polar environment of glycerol so much that only emission from the $S_{1,np}$ state can be observed. The points included in Figure 2 show clearly how different the emission in glycerol is from that in dioxane–water mixtures.[15]

Our approach to the analysis of fluorescence emissions of ANS compounds (and, by implication, many other probe molecules) is to identify specific excited states and apply stringent tests to confirm our assignments. For biochemical and biological applications, it seems likely that this precise understanding of probe behavior will be more helpful than nonspecific references to "general solvent polarity" or uninterpretable correlations with the quasi-macroscopic Lippert–Mataga equation.[16]

Knowledge of the fluorescence mechanisms along with the ρ value which allow us to evaluate substituent effects should make it possible to design ANS derivatives with properties appropriate for many needs.

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References and Notes

(1) (a) Tel-Aviv University; (b) State University of New York, Stony Brook, N.Y.
(2) A. Azzi, *Q. Rev. Biophys.*, **8**, 237–316 (1975).
(3) E. M. Kosower, "An Introduction to Physical Organic Chemistry", Wiley, New York, N.Y., 1968.
(4) E. M. Kosower and K. Tanizawa, *Chem. Phys. Lett.*, **16**, 419 (1972).
(5) D. C. Turner and L. Brand, *Biochemistry*, **7**, 3381 (1973).
(6) E. M. Kosower, H. Dodiuk, K. Tanizawa, M. Ottolenghi, and N. Orbach, *J. Am. Chem. Soc.*, **97**, 2167 (1975).
(7) E. M. Kosower and H. Dodiuk, *Chem. Phys. Lett.*, **26**, 545 (1974).
(8) F. C. Greene, *Biochemistry*, **14**, 747 (1975).
(9) H. Dodiuk and E. M. Kosower, *Chem. Phys. Lett.*, **34**, 253 (1975).
(10) R. P. Cory, R. R. Becker, R. Rosenbluth, and I. Isenberg, *J. Am. Chem. Soc.*, **90**, 1643 (1968).
(11) R. B. Freedman, D. J. Hancock, and G. Radda in "Probes of Structure and Function of Macromolecules and Membranes", Vol. 1, B. Chance, C-p. Lee, and J. K. Blasie, Ed., Academic Press, New York, N.Y., 1971.
(12) G. P. Sachdev, A. D. Brownstein, and J. S. Fruton, *J. Biol. Chem.*, **250**, 501 (1975).
(13) J. Shorter, "Correlation Analysis in Organic Chemistry: An Introduction to Linear Free Energy Relationships", Clarendon Press, Oxford, 1973, p 14.
(14) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, N.Y., 1969, p 294.
(15) E. M. Kosower and H. Dodiuk, *J. Am. Chem. Soc.*, **96**, 6195 (1974).
(16) E. Lippert, *Z. Naturforsch. A*, **10**, 541 (1955).
(17) N. Mataga, Y. Kalfu, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **28**, 690 (1955).
(18) Maximum was resolved from a shoulder.
(19) H. Dodiuk and E. M. Kosower, *J. Am. Chem. Soc.*, in press.

Infrared Spectra of *N*-Aryl Imines of *o*-Hydroxybenzaldehyde between 2000 and 1500 cm^{-1}

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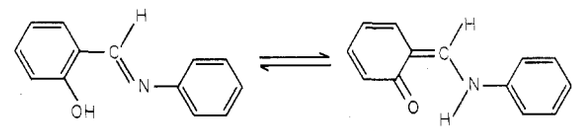
A thorough study of various protonic equilibria involving 2-[(phenylimino)methyl]phenol and other substituted aryl imines has been possible through the assignment of new infrared bands. In KBr, dimethyl sulfoxide, and fluorinated alcohols, $\nu_{C=O}$ and $\nu_{C=C}$ frequencies at 1640 and 1525–1547 cm^{-1}, respectively, were found, the result of an enol–keto tautomerism. In addition, in KBr and in 1,1,1,3,3,3-hexafluoro-2-propanol a $\nu_{C=NH^+}$ band was observed at 1627 cm^{-1}. Addition of the proton to the imine nitrogen in KBr is apparently intramolecular and precursory to keto formation. The effects of electron-withdrawing and -releasing groups on the equilibria were studied.

Introduction

The structure of *N*-aryl imines of benzaldehydes, viz., *N*-(phenylmethylene)benzenamine (I) and 2-[(phenylimino)methyl]phenol (II), has been widely studied. From studies in solution by optical[1–4] and ^{1}H NMR[5] spectroscopic techniques it has been clearly established that for II an enol imine–keto enamine tautomerism exists.



II

This tautomerism has been found to lie far on the enol