Intramolecular Donor–Acceptor Systems. 3. A Third Type of Emitting Singlet State For *N*-Alkyl-6-*N*-arylamino-2-naphthalenesulfonates. Solvent Modulation of Substituent Effects on Charge-Transfer Emissions

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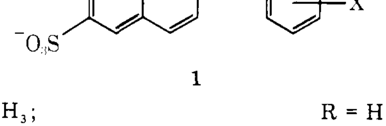
Abstract: Plots of the fluorescence maxima (as emission energies) for *N*-methyl-2-*N*-(X-phenylamino)-6-naphthalenesulfonates [**1**, R = CH_3; X = 4-Br, F, Cl, H, CH_3, OCH_3, 3-OCH_3, 3-CH_3, 3,5-$(CH_3)_2$] against the solvent polarity parameter, $E_T(30)$, for dioxane-water mixtures yield correlations which suggest emissions from $S_{1,np}$ and $S_{1,ct}$ states. Comparison of the extrapolated $S_{1,ct}$ emissions (in hydrocarbon solvent) for **1** with those for the compounds lacking the *N*-methyl group leads to the conclusion that the nonbonding electrons of the nitrogen are not conjugated to the positively charged phenyl in the $S_{1,ct}$ state, which therefore is $S_{1,ct(U)}$. Correlating emission energies/$2.303RT$ with the substituent constant σ^+ yields a ρ value of -25 ± 2, the highest ever noted for a solution process. The emission from the compound with H on nitrogen is assigned as arising from $S_{1,ct(C)}$ with new data confirming the original ρ value of -10.6 (C = conjugated; U = unconjugated). Other cases of isomeric charge-transfer states are cited. The ρ values correlating the energies of emissions from the $S_{1,ct(C)}$ and $S_{1,ct(U)}$ states exhibit a reasonably linear dependence on solvent polarity (as measured by the empirical parameter $E_T(30)$), the dependence being different for the two states. The more localized the charge in the emitting state, the greater the variation in the ρ value with solvent. The correlation coefficient of -38 ± 3 derived from the mass spectrometric data vs. σ^+ is assumed to reflect the interaction of a substituent with a unit charge; other ρ values may now be interpreted in a quantitative way.

Introduction

Precise characterizations of excited states (like other intermediates) are necessary if we are to understand their formation and behavior. Among the experimental data useful for such analyses are (1) emission energies and emission energy changes brought about by perturbation of the excited state through (a) substituent change or (b) solvent change; (2) quantum yields and quantum yield changes brought about by perturbations (a) or (b); (3) lifetimes and lifetime changes induced by perturbations (a) or (b); and (4) polarization of emissions and changes in polarization of emissions brought about by perturbations (a) or (b). Examination of the experimental results is guided by theory.

We have used emission energies and quantum yields along with excited state absorption spectra to show that a minimum of two singlet excited states, $S_{1,np}$ and $S_{1,ct}$ (np = nonplanar, ct = charge transfer) are required to account for the emissions from a series of 6-*N*-arylamino-2-naphthalenesulfonates (**1**, R = H) (ANS).[2-4] In connection with those studies, we examined also the corresponding *N*-methyl derivatives (**1**, R = CH_3). In viscous solvents like glycerol, the *N*-methyl compounds undergo a protonation reaction after irradiation, as we describe in detail elsewhere.[5] In fluid solvents, the behavior of the *N*-methyl derivatives is at first sight very similar to that of the compound with hydrogen bonded to nitrogen. The original work on *N*-methyl-6,2-ANS was conceived on this basis[6] and the application of *N*-methyl-6,2-ANS derivatives as fluorescent probes (e.g., for pepsin-substrate interaction[7]) is normally done as if the NH and NCH_3 compounds were similar in behavior. Nevertheless, examination of the emission energy vs. solvent polarity plots for the *N*-methyl-6,2-ANS compound carrying no substituent on the *N*-aryl group (**1**, R = CH_3; X = H) led to the realization that the extrapolated $E_{F,ct}$ value was much higher than expected. We therefore initiated and carried through a study of the emissions of *N*-methyl-6,2-ANS derivatives. Dynamic properties of the excited state obtained through lifetime measurements will be described separately.[8]



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R = CH_3;
X = 4-Br, Cl, F, H, CH_3, OCH_3
3-OCH_3, CH_3
3,5-$(CH_3)_2$

R = H
X = many substituents

Results

Synthesis. *N*-Methylanilines, if unavailable commercially, were synthesized by the specific procedure using methyl orthoformate.[9] The *N*-methyl-6-*N*-arylamino-2-naphthalenesulfonates were prepared by the Bücherer reaction.[10] All compounds (**1**, R = CH_3; X = 4-Br, Cl, F, H, CH_3, OCH_3, 3-OCH_3, 3-CH_3, 3,5-$(CH_3)_2$) were carefully purified and characterized by NMR, IR, and UV. High purity of the compounds studied is essential to the success of any careful analysis of fluorescence data.

Spectroscopic Measurements. Absorption spectra of *N*-methyl-6,2-ANS derivatives were almost insensitive to solvent and substituent effects, as previously found for the NH compounds.[3] Corrected emission spectra were obtained in all cases. Quantum yields were not corrected for changes in the refractive index of the solutions used. Emission data were recorded for all compounds in a series of dioxane-water solutions, as indicated in the tables. Data for six of the *N*-methyl-6,2-ANS derivatives are given in Table I. Table II shows data for an additional three derivatives with electron-supplying substituents.

The change in the position and appearance of the emission spectra as the solvent polarity changes is shown in Figure 1, in which the fluorescence spectra of the 3-methoxy derivative

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Table I. Emission Data for 6-*N*-Methyl-*N*-arylamino-2-naphthalenesulfonates in Dioxane–Water Mixtures[a,b]

Solvent % dioxane–water[c]	$E_T(30)$ value[d]	Substituent (ANS, **1**, X =) λ_{max}[e] (ϕ_F)[f]					
		4-F	4-Cl	4-Br[g]	3-OCH_3	3-CH_3	3-5-$(CH_3)_2$
99.9	36.3	413 (0.28)	416 (0.27)	414 (0.06)	424 (0.39)	410 (0.43)	411 (0.37)
99.6	37.0		418 (0.33)		425 (0.36)	412 (0.48)	412 (0.37)
99.1	38.5	416 (0.31)	420 (0.35)	416 (0.06)	426.5 (0.41)	415 (0.48)	414 (0.42)
98.1	41.1	419 (0.33)		418 (0.08)	429 (0.42)	418 (0.50)	417 (0.43)
97.2	42.0						
96.3	42.8	422 (0.34)	425 (0.37)	421 (0.09)	434 (0.41)	420 (0.48)	421 (0.46)
95.3	43.2	424 (0.35)		424 (0.08)	436 (0.38)		
94.4	44.2	426 (0.36)	428 (0.37)		439 (0.39)	423 (0.49)	423 (0.44)
92.5	45.6	428 (0.36)	430 (0.35)	426 (0.09)	442 (0.39)	424 (0.46)	424 (0.44)
90.6	46.5	429 (0.39)	432 (0.41)		444 (0.38)	426 (0.49)	426 (0.44)
85.9	47.8	430 (0.38)	434 (0.47)	428 (0.08)	446 (0.34)	427 (0.49)	427 (0.45)
81.3	48.7	431 (0.36)	435 (0.38)	430 (0.08)	448 (0.33)	428 (0.49)	428 (0.42)
76.6	49.7	432 (0.35)	437 (0.37)	432 (0.08)	455 (0.32)	429 (0.50)	429 (0.40)
71.9	50.5	434 (0.32)	439 (0.36)	434 (0.10)	460 (0.30)	430 (0.43)	430 (0.40)
67.2	51.3	436 (0.32)	442 (0.33)	436 (0.09)	465 (0.26)	431 (0.42)	433 (0.36)
62.5	52.0	438 (0.30)	446 (0.35)	438 (0.08)	470 (0.23)	434 (0.37)	436 (0.31)
57.8	52.6	440 (0.27)	451 (0.34)	439 (0.10)	475 (0.19)	438 (0.34)	440 (0.25)
53.1	53.2	442 (0.27)	458 (0.29)	440 (0.10)	480 (0.17)	442 (0.28)	446 (0.20)
48.4	53.9	444 (0.23)	466 (0.23)	441 (0.08)	485 (0.11)	446 (0.24)	452 (0.14)
43.2	54.9	448 (0.18)	474 (0.18)	444 (0.08)	488 (0.10)	452 (0.15)	458 (0.11)
39.1	55.8	454 (0.11)	479 (0.10)	448 (0.07)	496 (0.07)	456 (0.12)	462 (0.08)
34.4	56.5	458 (0.09)	484 (0.08)	455 (0.07)	504 (0.05)	462 (0.07)	466 (0.05)
29.7	57.2	465 (0.07)	490 (0.06)	468 (0.07)	510 (0.04)	468 (0.05)	470 (0.03)
25.3	57.9						
20.3	58.7	470 (0.04)	498 (0.04)	475 (0.03)	516 (0.02)	474 (0.02)	474 (0.02)
11.0	60.9	475 (0.02)	503 (0.03)	484 (0.02)	524 (0.03)	480 (0.01)	478 (0.01)
6.2	62.8			495 (0.01)			

[a] Temperature 25 ± 0.5 °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 measurement and the 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 C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11,** 1 (1968), or derived from values in that table by linear interpolation. [e] In nanometers. [f] ±10% or less, according to reproducibility. Quinine sulfate in 0.1 N H_2SO_4, $\phi_F = 0.55$. Yields are corrected for refractive index; solutions were not purged with nitrogen. [g] $E_T(30)$ values which apply to the solutions used are 0.1 kcal/mol greater in $E_T(30)$ range 36.3–50.5 and 0.4 kcal/mol greater in more polar solvents.

Table II. Emission Data for 6-*N*-Methyl-*N*-arylamino-2-naphthalenesulfonates in Dioxane–Water Mixtures[a]

Solvent % dioxane–water	$E_T(30)$ value[d]	4-CH_3	4-OC_6H_5	4-OCH_3
99.9	36.3	436 (0.43)	428 (0.43)	450 (0.10)
99.6	37.0		430 (0.41)	457 (0.18)
99.1	38.5	440 (0.74)	434 (0.62)	462 (0.16)
98.1	41.1	445 (0.70)	440 (0.70)	468 (0.16)
97.2	42.0			
96.3	42.8	449 (0.63)	448 (0.61)	474 (0.15)
95.3	43.2	455 (0.65)		478 (0.13)
94.4	44.2	459 (0.56)	456 (0.49)	482 (0.10)
92.5	45.6	465 (0.61)	462 (0.45)	485 (0.09)
90.6	46.5	470 (0.58)	468 (0.40)	490 (0.07)
85.9	47.8	474 (0.51)	470 (0.35)	495 (0.05)
81.3	48.7	478 (0.47)	472 (0.26)	495 (0.03)
76.6	49.7	482 (0.43)	475 (0.22)	500 (0.03)
71.9	50.5	486 (0.35)	472 (0.20)	
67.2	51.3	489 (0.31)	470 (0.14)	
62.5	52.0	493 (0.28)	475 (0.10)	
57.8	52.6	496 (0.20)	475 (0.08)	
53.1	53.2	500 (0.16)	475 (0.06)	
48.4	53.9			
43.2	54.9	504 (0.03)		
39.1	55.8	508 (0.01)		
34.4	56.5			
29.7	57.2			

[a] All footnotes of Table I apply.

Table III. Extrapolated Values for $S_{1,ct(C)}$ and $S_{1,ct(U)}$ Emissions for Hydrocarbon Solvent[a,b]

X	σ^+	$E_{F,ct(U)}$[c]	$E_{F,ct(C)}$[c]
4-Br	0.15	87.5	82.8
4-Cl	0.11	86.0	82.0
4-F	0.02[d]	86.8	80.0
3-OCH_3	0.12	82.4	81.2
H	0	84.0	78
3-CH_3	−0.07	81.3	79.7
3,5-$(CH_3)_2$	−0.14	79.1	
4-CH_3	−0.31	71.3	75.6
4-OCH_3.	−0.78	65.1	69.2
4-OPh	−0.36[e]	69.4	70.5

[a] $E_{T(30)} = 31$ kcal/mol. [b] See Figures 2–4 for illustration of extrapolations used. [c] Emissions in kcal/mol; approximate variation ±1.3–1.4 kcal/mol. [d] Based on ionization potential of benzyl radicals. [e] Two σ^+ constants are given by H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80,** 4979 (1958). The σ^+ constant of 0.36 appeared to us more reasonable and was used. Further work would be required to define more exactly the characteristics of the 4-phenoxy substituent.

(**1,** R = CH_3; X = 3-OCH_3) in a series of dioxane–water solutions are illustrated.

Treatment of Data. Fluorescence maxima, read from suitably amplified spectroscopic curves and converted to emission energies (kcal/mol), are plotted against the solvent polarity parameter, $E_T(30)$,[11,12] in Figure 2. Emission energies for the *N*-methyl and *N*-hydrogen (**1,** R = CH_3 and R = H; X = H) compounds are plotted against $E_T(30)$ in Figure 3 to reveal the clear difference between the two compounds. Even compounds which are experimentally quite similar to one another like the 3-methyl derivatives in both the *N*-methyl and *N*-hydrogen series can be differentiated in plots against $E_T(30)$ as shown

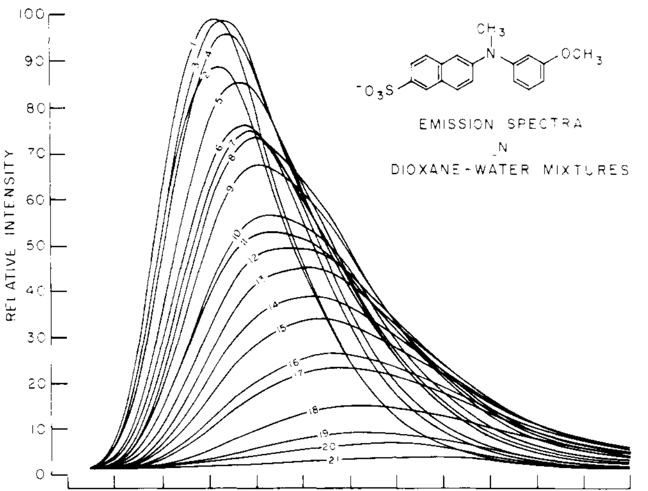


Figure 1. Fluorescence spectra for *N*-methyl-6-*N*-(3-methoxyphenylamino)-2-naphthalenesulfonate (**1**, R = CH_3: X = 3-OCH_3) in a series of dioxane-water solutions. Dioxane content (%) of the solutions used is 1, 99.9; 2, 99.6; 3, 99.1; 4, 98.1; 5, 96.3; 6, 95.3; 7, 94.4; 8, 92.5; 9, 90.6; 10, 85.9; 11, 81.3; 12, 76.6; 13, 71.9; 14, 67.2; 15, 62.5; 16, 57.8; 17, 53.1; 18, 48.4; 19, 43.2; 20, 34.4; 21, 20.3.

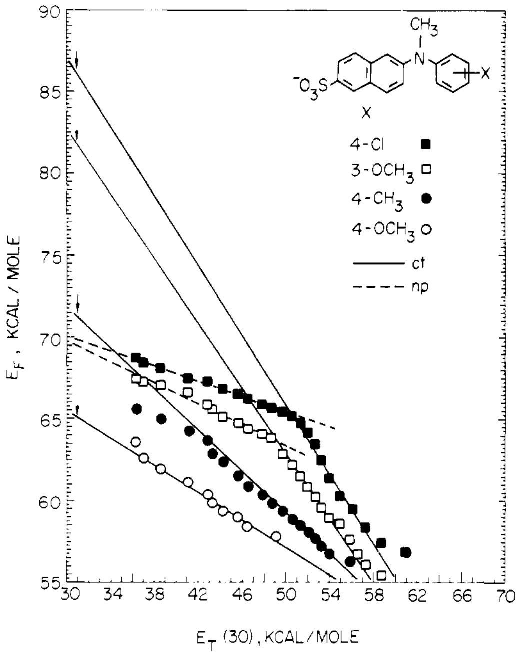


Figure 2. A plot of emission energy (E_F) for a series of *N*-methyl-2-*N*-arylamino-6-naphthalenesulfonates (**1**, R = CH_3; X = 4-Cl, CH_3, OCH_3, 3-OCH_3) against $E_T(30)$ (kcal/mol), the solvent polarity parameter, for a series of dioxane-water mixtures. The extrapolations to hydrocarbon solvents are shown to illustrate the method of obtaining emission energies under nonsolvating conditions ($E_{F,ct,extrapolated}$). Linear correlations for the np emissions of the 4-Cl and 3-OCH_3 compounds are also shown.

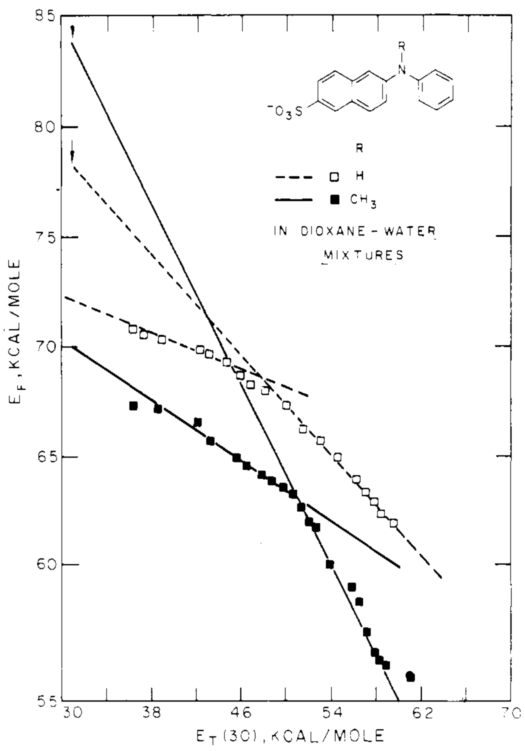


Figure 3. A plot of emission energy (E_F, kcal/mol) for *N*-methyl-6-*N*-phenylamino-2-naphthalenesulfonate (**1**, R = CH_3; X = H) and 6-*N*-phenylamino-2-naphthalenesulfonate (**1**, R = H; X = H) against $E_T(30)$ (kcal/mol), the solvent polarity parameter, for a series of dioxane-water solutions. Extrapolation of the lines assigned to the charge-transfer emissions yields rather different results in the two series.

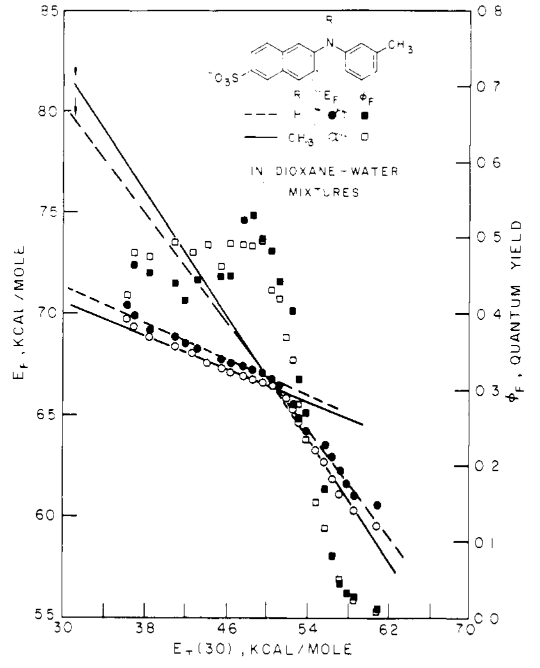


Figure 4. A plot of emission energy (E_F, kcal/mol) and quantum yield (ϕ_F) for *N*-methyl-6-*N*-(3-methylphenylamino)-2-naphthalenesulfonate (**1**, R = CH_3; X = 3-CH_3) and 6-*N*-(3-methylphenylamino)-2-naphthalenesulfonate (**1**, R = H; X = 3-CH_3) against $E_T(30)$ (kcal/mol), the solvent polarity parameter, for a series of dioxane-water solutions. Extrapolation of the line assigned to the charge-transfer emissions leads to readily distinguishable energies for the charge-transfer emissions in nonpolar, hydrocarbon solvent.

in Figure 4. The values for the emission energies obtained by extrapolation to hydrocarbon solvent [$E_T(30) = 31$] are listed in Table III. The minimum and maximum correlation lines yield extrapolated E_F values varying by ±1.3–1.4 kcal/mol or ±1.0 kcal/mol for $E_F/2.303RT$.

Discussion

One of the most effective and practical ways of evaluating the effects of solvents on emission processes is that of comparison with an empirical solvent polarity parameter like *Z* value or $E_T(30)$.[13] These parameters are based on well-defined charge-transfer processes; the molecules or ion pairs within which the charge-transfer transitions occur act, in a sense, like analog computers, translating the sum of solvent interactions

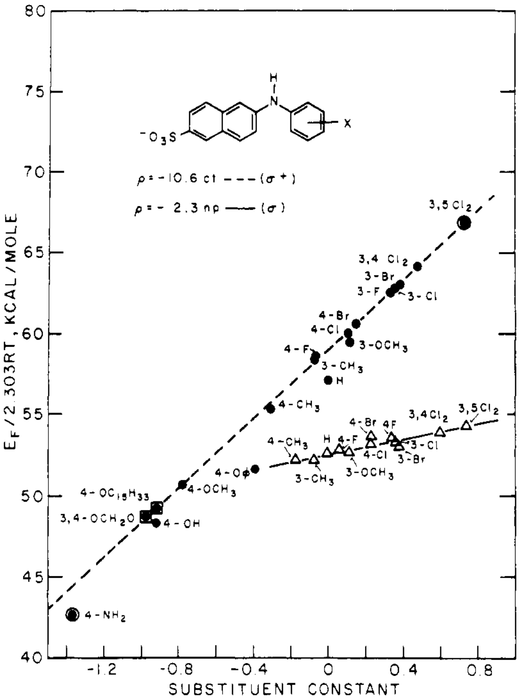


Figure 5. A plot of extrapolated E_F (emission energies)/2.303*RT* against σ (Hammett substituent constants) (low slope line, $\rho = -2.3$) or σ^+ (Hammett-Brown substituent constants) (high slope line $\rho = -10.6$) for a series of 6-*N*-phenylamino-2-naphthalenesulfonates (**1**, R = H; X = substituent or substituents as indicated in the figure). The extrapolated emission energies were obtained from emission energy (E_F) vs. $E_T(30)$ plots from measurements of emission maxima made in dioxane-water solutions except as follows. Extrapolations for a number of ANS derivatives with strong electron-withdrawing groups (**1**, R = H; X = 3-Br, 3-Cl, 3-F, 3,4-Cl_2) were made on the correlation lines for E_F vs. $E_T(30)$ plots based on measurements made in 1,2-ethanediol-water solutions. The extrapolated value for the 3,5-dichloro-ANS derivative (**1**, R = H; X = 3,5-Cl_2) was estimated from the line used after noting that the measured value in water fell exactly on the ρ value correlation for that solvent polarity. The extrapolated value for the 4-amino-ANS derivative (**1**, R = H; X = 4-NH_2) was measured in pure dioxane (λ_{max} 520 nm, $\phi_F = 4 \times 10^{-3}$). The emission energy/2.303*RT* fell almost exactly on the correlation line for E_F/2.303*RT* in $E_T(30) = 36$. It was thus deemed reasonable to place the point on the line shown in the figure at the σ^+ value used for the $E_T(30)$ correlation line. The two points obtained from single measurements at different solvent polarities are marked with a circle (◎). The points for the methylenedioxy-ANS (**1**, R = H; X = 3,4-OCH_2O) and 4-hexadecyloxy-ANS (**1**, R = H; X = 4-$C_{16}H_{33}O$) were placed on the line in order to obtain their σ^+ values and are marked with a square (▣). The values of E_F/2.303*RT* are ca. ±1.0 kcal/mol (see text).

on the probe molecule into easily measured excitation energies. The theoretical model for the effect of solvent upon such transitions (those in which charge separation disappears through light absorption)[13] permits a quantitative estimate of the interaction between the ion-pair form and the solvent. Plotting emission energies against the appropriate parameter[11] permits (a) a rapid evaluation of whether or not a charge-transfer process is involved, with slopes greater than 0.5 suggesting charge transfer; (b) prediction of the emission energy in the absence of solvation; (c) decision on the number of different emitting states; (d) some quantitative idea of the solvation energies involved in the stabilization of the different emitting states and therefore of the dipole moments of those states.

The emission energies for some of the ANS derivatives we wish to examine in the present study are plotted against the solvent polarity parameter, $E_T(30)$, in Figures 2-4. Two correlation lines are immediately evident for almost every set of data. On the basis of the slopes, these are readily assigned to (a) $S_{1,np} \rightarrow S_{0,np}$ and (b) $S_{1,ct} \rightarrow S_{0,np}$ transitions.[3] The $S_{1,np}$ state is one in which the excitation is localized on the naphthalene ring; the $S_{1,ct}$ state is a charge-transfer state in which an electron has been transferred from the aryl group to the naphthalene ring. The equilibrium forms of both the $S_{1,np}$ and $S_{1,ct}$ states have aryl groups located in planes which are perpendicular to the plane of the naphthalene ring. Quantum yields similarly exhibit two types of response to solvent change, but are illustrated only in the case of the 3-methyl derivative (Figure 3). Quantum yields are also influenced by the heavy atom effect, which will be discussed elsewhere. The general similarity of NH and NCH_3 derivatives with respect to the effect of solvent polarity provides clear evidence against a trivial explanation like "differential hydrogen bonding" for the behavior of the $S_{1,np}$ and $S_{1,ct}$ states in emission. Substituent effects also strongly support the interpretation that two different emitting states are involved.

We have previously found that the viscous solvent, glycerol, inhibited the $S_{1,np} \rightarrow S_{1,ct}$ conversion, so that emission from $S_{1,np}$ was observed in the polar glycerol.[3,14] Extrapolation of the line correlating emission energies assigned to the $S_{1,np}$ state to the solvent polarity for glycerol ($E_T(30) = 57.0$ at 25 °C) yields an emission energy close to that found experimentally.[14] We have applied this test to the unsubstituted *N*-methyl compound (**1**, R = CH_3; X = H) with the predicted λ_{max} being 468 nm rather than the experimental value of 470 nm. There is little doubt that the fluorescence spectrum is largely the result of emission from the $S_{1,np}$ state, in view of the expectation that emission from the $S_{1,ct}$ state would have had a maximum at 498 nm (cf. Figure 1, ref 5).

To minimize the effect of interaction with the solvents, the correlation lines are extrapolated to $E_T(30) = 31$, the polarity for a hydrocarbon solvent like hexane. In the case of the N-H ANS derivatives (**1**, R = H), the extrapolated emission energies are utilized to evaluate substituent effects (Table III). The emission energies are divided by 2.303*RT* to scale them correctly for the Hammett-Brown substituent constants, then plotted against either σ (for emissions from the $S_{1,np}$ state) or σ^+ (for emissions from the $S_{1,ct}$ state). The correlations are amazingly good and the slopes have remained essentially unaltered by the addition of many new points to the original correlations[3] as shown in Figure 5 (ρ_{ct} −10.6; ρ_{np} −2.3).

As pointed out in the Introduction, the extrapolated $E_{F,ct}$ for the *N*-methyl-ANS compound was higher than that for the compound with hydrogen on nitrogen (**1**, R = H). The difference was unexpected, since *N*-methyl is normally electron donating and it was thought that the positive charge in the aryl ring should be stabilized by an *N*-alkyl substituent thus lowering the emission energy for the state. We inferred from this result that the aryl ring was not conjugated to the nitrogen in the charge-transfer state, so that the stabilization expected from the *N*-methyl group could not be effective. However, a positive charge localized in the aryl ring should be more responsive to the effects of substituents on the aryl ring, i.e., the ρ value should be greater than found for the case of NH compounds. In fact, a plot of extrapolated $E_{F,ct}$ energies against σ^+ yielded a rather good correlation with a ρ value of −25 (Figure 6).

The high ρ value was plausible only in terms of the supposition that the charge was more localized in the aryl ring. We illustrate the structures proposed for the equilibrium states in Figure 7, with the assignments for the charge-transfer states now further specified by whether or not the aryl ring is conjugated with nitrogen. When conjugated, as in the case of N-H ANS derivatives, the state is $S_{1,ct(C)}$; for the *N*-methyl compounds, for which our evidence now suggests that the aryl ring is not conjugated with the nitrogen, the state is labeled $S_{1,ct(U)}$.

On the basis of the present work and that previously published, we can summarize the photophysical behavior of the

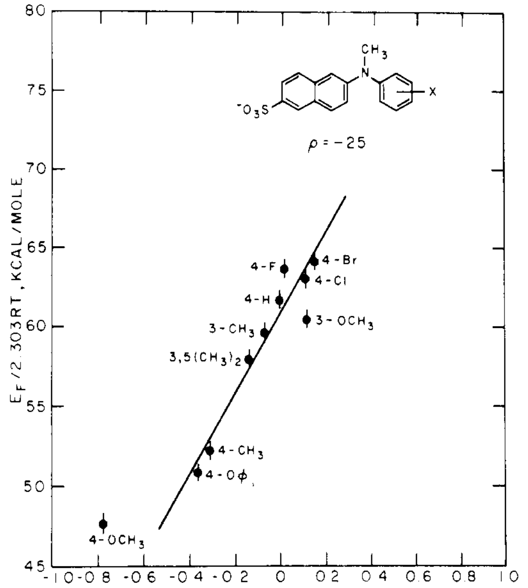


Figure 6. A plot of extrapolated charge-transfer energies divided by 2.303*RT* against the substituent constant, σ^+. The point for the 4-CH$_3$O group was not included in drawing the correlation line which corresponds to a ρ-value of -25 ± 2. A σ^+ of $+0.02$ was used for 4-F as derived from the ionization potential for benzyl radicals (see ref 13). The error bars shown in the figure correspond to ±1.0 kcal/mol.

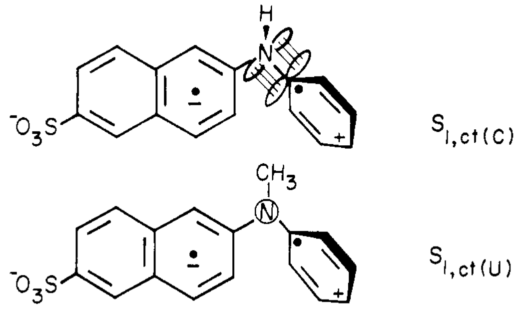


Figure 7. Structures of two different charge-transfer states assigned as the origins of the charge-transfer emissions for 6-*N*-arylamino-2-naphthalenesulfonates (**1**, R = H) ($S_{1,ct(C)}$) and *N*-methyl-6-*N*-arylamino-2-naphthalenesulfonates (**1**, R = CH$_3$) ($S_{1,ct(U)}$). The equilibrium forms are illustrated; emission may occur from nonequilibrium forms, e.g., those involving some librational motion of the aryl groups.

6,2-ANS system as shown in eq 1, and that of the *N*-methyl-

$$\begin{tikzcd}
T_{1,np} \arrow[d] & S_{1,np} \arrow[l] \arrow[rr, shift left] \arrow[dr] & & S_{1,ct(C)} \arrow[ll, shift left] \arrow[d] \\
h\nu_P & S_{0,np} \arrow[u] & h\nu_{F,np} & h\nu_{F,ct}
\end{tikzcd} \qquad (1)$$

6,2-ANS system in eq 2. It should be noted that the conversion

$$\begin{tikzcd}
T_{1,np} \arrow[d] & S_{1,np} \arrow[l] \arrow[rr, shift left] \arrow[dr] & & S_{1,ct(U)} \arrow[ll, shift left] \arrow[d] \\
h\nu_P & S_{0,np} \arrow[u] & h\nu_{F,np} & h\nu_{F,ct}
\end{tikzcd} \qquad (2)$$

of the $S_{1,np}$ state to the $S_{1,ct}$ state is reversible.[3]

It was possible to extract, from the linear correlations of E_F vs. $E_T(3)$, the emission energies at specified solvent polarities. The emission energies, divided by 2.303*RT*, were plotted against σ^+, as illustrated in Figure 8. The ρ values at different solvent polarities are indicated in the figure. Similar correlations of $E_F/2.303RT$ vs. σ^+ were obtained for 8,1-ANS derivatives and will be discussed elsewhere.[15]

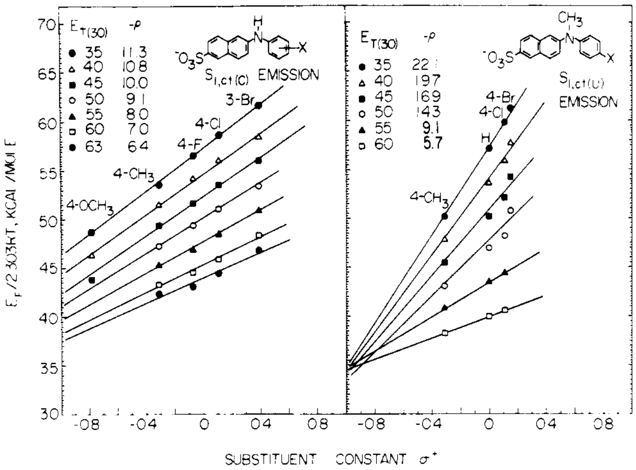


Figure 8. Left: A plot of emission energies divided by 2.303*RT* from the $S_{1,ct(C)}$ state of 6-*N*-(X-phenylamino)-2-naphthalenesulfonates vs. σ^+, the substituent constant, for a series of dioxane–water mixtures, as indicated in the figure. The slopes are the ρ values. Right: A plot of emission energies divided by 2.303*RT* from the $S_{1,ct(U)}$ state of *N*-methyl-6-*N*-(X-phenylamino)-2-naphthalenesulfonates vs. σ^+, the substituent constant, for a series of dioxane–water mixtures, as indicated in the figure. The slopes are the ρ values.

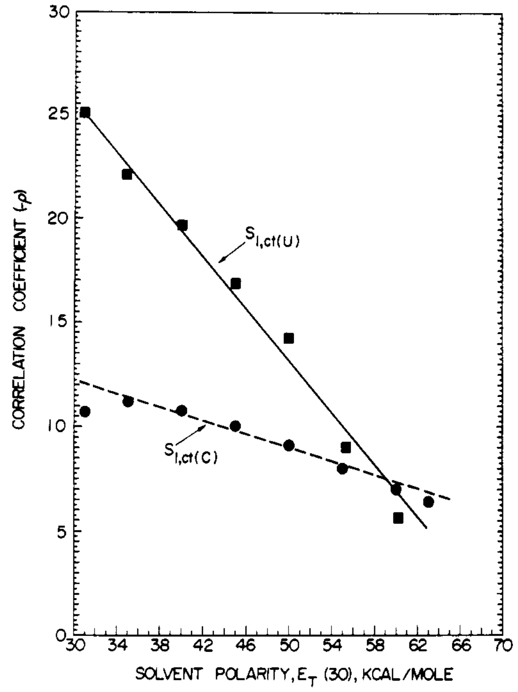


Figure 9. A plot of ρ values for $S_{1,ct(C)}$ (- - - - - -) and $S_{1,ct(U)}$ (—) emissions vs. the solvent polarity parameter, $E_T(30)$. The ρ values were derived from the plots shown in Figure 1. The difference between the solvent sensitivities of the two emissions is very large.

The ρ values derived from the linear correlations shown in Figure 8 are plotted against $E_T(30)$ in Figure 9, revealing rather good correlations for the values from both $S_{1,ct(U)}$ and $S_{1,ct(C)}$ states.

The magnitude of the ρ value is a measure of the electron demand upon the substituents in the reaction.[16] An ionization process should make the largest demand upon a substituent; in addition, the smaller the degree of delocalization the greater the demand on the substituent. These two trends find maximum expression in the process discovered by Taft and coworkers:[17]

$$CH_3X + e^- \rightarrow {}^+CH_2X + H + 2e^- \qquad (3)$$

for which a ρ value of -38 ± 3 can be estimated by a plot of the reported stabilization energies divided by $2.303RT$ against σ^+. Greater delocalization in the cation, as in the ionization of benzyl radicals,[18] leads to $\rho = -19$; correcting for stabilization of the radicals (estimated as $\rho = +2$),[19] the ρ value for the stabilization of the cation is about -17. Streitwieser and co-workers[20] have calculated the energetics of the transformation $ArCH_3 \rightarrow ArCH_2^+$ as having a linear relationship to σ^+, with a ρ value between -19 and -22. Both experimental measurements and theoretical calculations led to a ρ of ~ -24 for the proton affinities of substituted benzenes.[21] Traylor[22] has determined the ρ value for the charge-transfer absorptions of complexes between tetracyanoethylene (TCNE) and aromatic compounds, for which a value of -21 for the stabilization of the charge-transfer state in hydrocarbon solvent may be estimated after correcting with the ρ (+4) for stabilization of the ground state.[23] (See below.) We have found that the ρ value for the charge-transfer emission from the $S_{1,ct(U)}$ state of N-methyl-6,2-ANS derivatives in hydrocarbon solvents is ca. -25. Estimating[23] ρ for the stabilization of the ground-state aryl group as +4, the ρ for the stabilization of the aryl cation radical in the charge-transfer state is -21.

It seems clear that there is a pattern to these estimates for the ρ values of various processes which is difficult to escape. First, the highest ρ value is -38, that for charge on a single center. Second, delocalization within one aromatic ring of a positive charge leads to a ρ value of ca. -21. Third, delocalization in a benzyl cation is associated with a ρ value of ca. -18.

Quantitative Consideration. A number of questions, including that which is a theme of this article (solvent modulation of substituent effects), are better discussed in quantitative rather than qualitative terms. We shall therefore adopt a naive but completely straightforward and simple interpretation of the ρ values. Our justification for the approach rests upon the following points: (1) close correlation with what a chemist understands about the nature of substituent effects, i.e., net interaction of the substituent with charges near the substituent; (2) remarkable correspondence among ρ values of different origin based on species within which similar charge distributions might be expected; (3) close correspondence to calculated charge distributions;[20,21] (4) clarity in considering radiative rate changes with solvent polarity.[24]

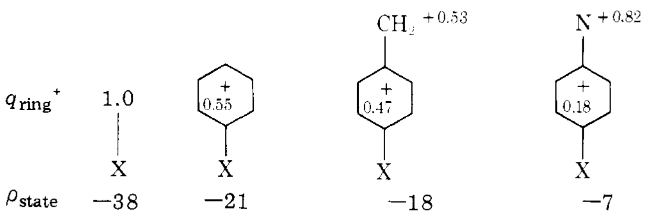
We make the simple calculation, according to the expression of eq 4a, for the fraction of a unit charge which the substituent probes within the aromatic ring. For emissions or absorptions, the q_{ring} signifies the change in the fraction of charge in the ring on going from the initial to the final state (eq. 4b).

$$q_{\text{ring}} = \rho_{\text{state}}/\rho_{\text{maximum}} \tag{4a}$$

$$q_{\text{ring change}} = \rho_{\text{transition}}/\rho_{\text{maximum}} \tag{4b}$$

$$\text{with } \rho_{\text{maximum}} = -38$$

Streitwieser and co-workers[20] have shown that the calculated charges on the CH_2 group (0.4^+) of a benzyl cation change very little with very substantial changes in the electron-donating or electron-accepting character of the substituent. The charges thus obtained through eq 4 are indicated in the formulas below.



The variations in ρ value with solvent which are usually referred to are relatively small (e.g., from 1.0 to 2.3 for C_6H_5COOH dissociation, H_2O to C_2H_5OH,[25] from 0.84 to 2.2 for $C_6H_5COOH + (C_6H_5)_2CN_2$ reaction, CH_3OH to $C_6H_5CH_3$,[26,27] and -2.1 to -3.1 for the reaction of $C_6H_5N(CH_3)_2$ with $CH_3OC_6H_2(NO_2)_3$, CH_3OH to CS_2[28]).

Two examples will suffice to show how useful correlation of the ρ value with solvent polarity can be. We alluded above to the ρ value estimated for the charge-transfer absorption maxima of TCNE complexes of aromatic hydrocarbons in hydrocarbon solvent:

$$ArH + TCNE \rightleftharpoons ArH,TCNE \xrightarrow{h\nu} ArH^{+\cdot},TCNE^{-\cdot} \tag{5}$$

The experimental value found by Traylor et al.[22] is -19 for complexes formed in dichloromethane solvent. The $E_T(30)$ value for dichloromethane is 41.1. Locating the point for $-\rho$ of 19 at the $E_T(30)$ value for dichloromethane, we find that it falls almost exactly on the line drawn for the $S_{1,ct(U)}$ ρ values. Since the charge distribution and substituent effects in both ground and excited states for the charge-transfer emission should resemble those for the charge-transfer absorption, we may guess that the effect of solvent on the ρ value in the two cases should be parallel. In the absence of additional experiments, we expect a ρ value for the absorption maxima in hydrocarbon solvent for the ArH-TCNE complexes to be about -25. Measurements to confirm this expectation would certainly be of interest.

The ρ value for the solvolysis of the *tert*-cumyl chlorides in 90% acetone-water[29] is -4.54, and has apparently not been obtained for any other solvent polarity. The $E_T(30)$ value for 90% acetone-water is 50.3;[12] if we assume that the ρ value represents the effect of the substituent on the transition state, and that the carbonium ion is half formed at that point (eq 5), the ρ value for a fully formed carbonium ion should be -9.1 under these conditions. Locating the point for -9.1 and 50.3 on the ρ value vs. solvent polarity plot, we note that the point falls almost exactly on the line for $S_{1,ct(C)}$ ρ values. Again, experimental confirmation of the conclusion that the $S_{1,ct(C)}$ emission energies should exhibit substituent effects with ρ values twice those of the solvolysis of *tert*-cumyl chlorides would be valuable.

Experimental Section

Syntheses. N-Methylanilines were prepared from the corresponding anilines with methyl orthoformate[9] and their structures were confirmed by NMR. N-Methyl-6-N-phenylamino-2-naphthalenesulfonate (**1**, R = CH_3; X = H) was prepared by the method of Cory et al.,[6] as detailed elsewhere.[5] Other derivatives were prepared in a similar way and purified, in the usual case, by column chromatography on silica (eluent benzene-methanol, 85:15), followed by crystallization from 10% NaOH. Purity was confirmed by TLC and structures were established by NMR and UV.

UV: three absorption bands (solvent, dioxane or ethanol) representing excitation to S_1, S_2, and S_3 at 360, 320 (280, sh), 260 nm. Absorption coefficients varied somewhat with substituent, to S_1 (4000-7000), S_2 (15 000-30 000), S_3 (15 000-35 000). Absorption spectra are given by Cory et al.[6] and Brand et al.[30]

NMR (Me_2SO): aromatic H naphthalene, aryl [δ 6.6-8.5 (m)], N-Me [δ 3.4-3.5 (3 H, s), obscured by D_2O in several cases]; groups 4-CH_3, δ 2.3 (3 H, s); 3-CH_3, 2.35 (3 H, s); 3,5-$(CH_3)_2$, 2.35 (6 H, s); 4-OCH_3, 3.9 (3 H, s); 3-OCH_3, 3.8 (3 H, s); OC_6H_5, 7-8, mixed with other aromatic protons.

Spectra. Absorption spectra were measured with a Cary Model 17 spectrophotometer. Fluorescence spectra were measured with a Perkin-Elmer Hitachi Model MPF-4 spectrofluorimeter with a corrected spectra attachment, with quantum yields referred to quinine sulfate in 0.1 N H_2SO_4 as 0.55. Solutions were not purged with nitrogen since the shape of the emission curves is not affected and the quantum yields of fluorescence only slightly increased in nonpolar solvents (unchanged in medium- and high-polarity solvents) by such purging. Sample temperatures were controlled at 25.0 ± 0.5 °C. Dioxane was from E. Merck, Darmstadt (spectrograde). Plots were executed with a Hewlett-Packard 9810-9862 calculator-plotter combination.

Acknowledgment. The support of the United States–Israel Binational Science Foundation (BSF) is appreciated.

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(1) (a) Tel-Aviv University; (b) State University of New York, Stony Brook.

(2) Previously, we numbered the *N*-arylamino group as 2-, but we have accepted the editorial suggestion that 6- is more appropriate and conforms more closely to accepted nomenclature.

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Intramolecular Donor–Acceptor Systems. 4. Solvent Effects on Radiative and Nonradiative Processes for the Charge-Transfer States of *N*-Arylaminonaphthalenesulfonates

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Abstract: Fluorescence lifetimes and fluorescence quantum yields for 6,2- and 8,1-*N*-arylaminonaphthalenesulfonates (ANS) have been measured in dioxane-water solutions having a wide range of solvent polarities, as measured by the empirical solvent polarity parameter, E_T(30). The radiative rate constants for change-transfer emission ($S_{1,ct} \rightarrow S_{0,np}$) and the nonradiative rate constants for electron-transfer reaction ($S_{1,ct} \rightarrow S_{0,np}$) are both sensitive to solvent. The greater sensitivity of the latter, k_{nr}, than the former, k_r, to changes in solvent polarity accounts for the strong quenching observed for ANS derivatives in polar solvents. The solvent dependence of $(k_r)^{1/2}$ can be accounted for reasonably well in terms of a relationship based on substituent effects on emission energies. The linear dependence of the transition state free energy $\Delta G^{\ddagger}$ (for k_{nr}) on E_T(30) is explained by the "migration" of charge (i.e., screening) into the solvent shell. The $\Delta G^{\ddagger}$ correlations for many of the ANS derivatives extrapolate to a common region, which corresponds roughly to the dielectric relaxation rate for water. The intramolecular electron-transfer rate is thus limited by a property of a suitable reaction field, R_s, in the solvent, with intramolecular factors such as donor–acceptor overlap and bond distance changes all being compatible with still higher electron-transfer rates. A mechanism for an intramolecular electron-transfer reaction is thus established. The relationship of the strong solvent effect on emission energies to the strong effect upon $\Delta G^{\ddagger}$ is explained. Analysis of other results from the literature, using the ANS results for k_r and k_{nr} as references, reveals that some quenching reactions may be electron transfer and some most certainly are not. A new quenching mechanism, formation of an unstable covalent bond, is proposed for several molecules. A classification of decay processes for excited charge-transfer states is also given.

Introduction

In 1954, Weber and Laurence[2] made the discovery that certain arylaminonaphthalenesulfonates (ANS), highly fluorescent in nonpolar solvents, were strongly quenched in very polar solvents like water. The application of the phenomenon to the measurement of protein binding site polarity[3] stimulated several studies[4,5] which, however, did not lead to an explanation for the solvent effect. Even sophisticated investigations like

0002-7863/78/1500-4179$01.00/0