# Intramolecular Donor–Acceptor Systems. 9. Photophysics of (Phenylamino)naphthalenesulfonates: A Paradigm for Excited-State Intramolecular Charge Transfer

EDWARD M. KOSOWER

Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel 69978, and Department of Chemistry, State University of New York, Stony Brook, New York 11794

Many isomeric (phenylamino)naphthalenesulfonates were prepared as dye intermediates[1] during the late nineteenth century; they include the 8-(phenylamino)-1-naphthalenesulfonate (8,1-ANS, **1**) and 6-(phenylamino)-2-naphthalenesulfonate (6,2-ANS, **2**) salts.[2] In 1954 Weber and Laurence[3] discovered that
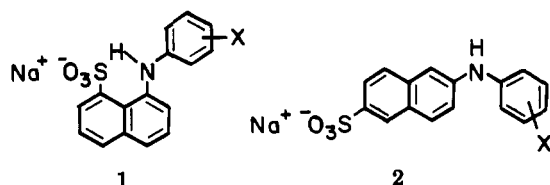
1 and **2** are very weakly fluorescent in water but brightly fluorescent when combined with albumin, dissolved in nonpolar organic solvents, or isolated in solid form. The environment-sensitive fluorescence caught the fancy of many interested in biological problems, and the ANS derivatives were used to measure the binding capacity of serum albumin,[4] to evaluate "polarity" of protein and enzyme binding sites,[5-7] and to observe nerve action potentials optically.[8] An extensive study of some photophysical properties of amino- and (phenylamino)naphthalenesulfonates did not lead to an explanation of the solvent sensitivity of the fluorescence.[9]

We thought that a thorough analysis of the ANS fluorescence would allow us to design more effective optical probes for nerve action. Our studies of ANS photophysics have yielded rich scientific rewards, even though effective ANS probes for nerves were not forthcoming. I should mention that the empirical selection of optical nerve probes[10] has led to a number of useful compounds; an electrochromic dye chosen on theoretical grounds promises to revitalize the analytical approach.[11]

Two Fluorescent States. A detailed study of solvent effects on the fluorescence properties of 6,2-ANS derivatives led us to a specific conclusion, namely, that the central feature of the photophysics of all (phenyl-

Table I
Absorption and Emission Maxima of 6-(4-X-phenylamino)-2-naphthalenesulfonates

solvent	E_T-(30) value[a]	λ_{max}, (ϵ or ϕ_F) nm X = H	X = CH_3	X = F
		Absorption		
EtOH	51.9	358 (5300)	360 (5600)	360 (4600)
H_2O	63.2	355 (5100)	357 (5000)	355 (4100)
		Fluorescence		
99.6%[b]	37.1	406 (0.57)		
99.1%	38.5		414 (0.43)	407 (0.60)
76.6%	49.7		441 (0.28)	424 (0.65)
75.4%	49.9	425 (0.59)		
26.2%	57.7	458 (0.05)		
25.3%	57.9		474 (0.01)	459 (0.06)

[a] Solvent polarity parameter. [b] % dioxane in dioxane-water v/v.

amino)naphthalenesulfonates is that there are two fluorescent states which differ in response to solvent and substituent change. The existence of the two states was first revealed by plots of the fluorescence emission energies (E_F) as a function of solvent polarity, in which the correlations exhibit two slopes.[12,13] How can one judge the effect of solvent polarity?

Evaluation of solvent-sensitive properties requires well-defined reference parameters. A macroscopic parameter, dielectric constant, does not alwasys give interpretable correlations of data. The first microscopic measure of solvent polarity, the Y value, based on the solvolysis rate of *tert*-butyl chloride,[14] is particularly valuable for correlating solvolysis rats. Y values are tedious to measure, somewhat complicated in physical basis, and characterizable for a limited number of solvents. The Z value, based on the charge-transfer electronic transition of 1-ethyl-4-carbomethoxy-pyridinium iodide,[15,16] is easy to measure and has a

Edward M. Kosower, a native of Brooklyn, NY, attended Stuyvesant High School and the Massachusetts Institute of Technology before undertaking graduate work at the University of California, Los Angeles, where he obtained the Ph.D. in 1952 (with the late Saul Winstein). He was an N.I.H. Postdoctoral Fellow at Basel (with C. A. Grob) and at Harvard (with F. H. Westheimer) and was successively a member of the faculty of Lehigh University, University of Wisconsin, and the State University of New York, Stony Brook, before accepting his present position at Tel-Aviv University. He remains Adjunct Professor Chemistry at S.U.N.Y., Stony Brook. Edward Kosower's research interests include solvent polarity parameters (Z values), isolable but reactive intermediates (e.g., pyridinyl radicals, monosubstituted diazenes), thiol-oxidizing agents, membrane mobility agents, intramolecular electron-transfers, novel heterocyclic systems (especially the bimanes), fluorescent-labeling agents, and the theory of biological receptor mechanisms.

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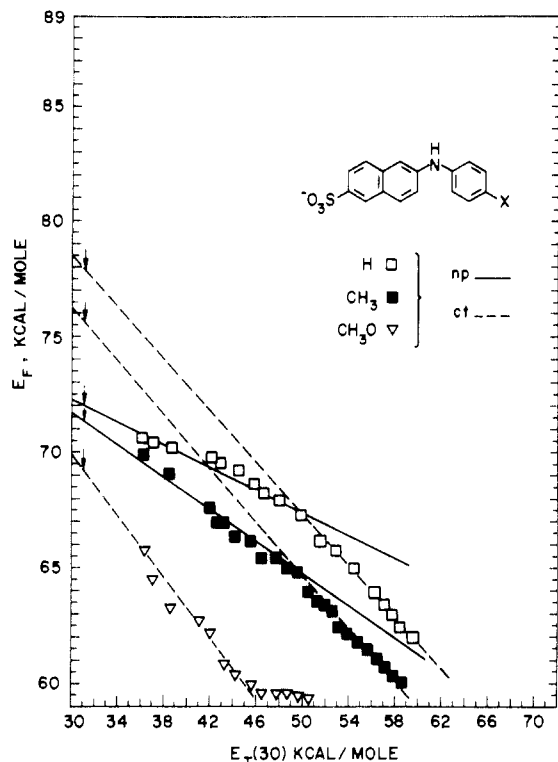(15) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253–3261.

Figure 1. A plot of fluorescence maxima (as E_F) vs. the solvent polarity parameter, $E_T(30)$ for three 6-(phenylamino)-2-naphthalenesulfonates (2, 4-X = H, CH$_3$, CH$_3$O) in a series of dioxane–water mixtures. The solid lines correlate the $S_{1,np}$ emissions; the dashed lines correlate the $S_{1,ct}$ emissions. The arrows indicate the extrapolated emission energies for the states in hydrocarbon solvent ($E_T(30)$ = 31). The failure of the maximum for the 4-CH$_3$O derivative to shift to longer wavelengths in solvents with a polarity greater than $E_T(30)$ > 47 is probably due to a contribution of flurescence from a protonated form (λ_{max} 405 nm), which balances the expected shift to longer wavelengths for the $S_{1,ct}$ emission. (Cf.: Dodiuk, H.; Kosower, E. M. *J. Am. Soc.* **1977**, *99*, 859) (reprinted from ref 13).

readily understandable physical origin. However, nonpolar solvent *Z* values are difficult to obtain because of low salt solubility. The $E_T(30)$ value of Dimroth and Reichardt[17,18] is based on an intramolecular charge-transfer transition in a pyridinium phenol betaine which dissolves in almost all solvents. We have used the $E_T(30)$ value in the studies of ANS derivatives as the measure of solvent polarity. Solvent polarity is what is measured by a particular technique and may refer to different summations of molecular properties in different cases. For this reason, only simple reference processes should be used to derive solvent parameters.

Having considered the question of how to evaluate solvent polarity, we can now look at the results of fluorescence measurements in solvents of different polarities. The energies corresponding to the maxima of the fluorescence spectra (Table I) for 2 in a graded series of dioxane–water mixtures are plotted against the $E_T(30)$ value (Figure 1). Two correlation lines are proof of two different behaviors. Since one excited state could not account for two lines, we conclude that the fluorescence of 2 arises from two different excited states. The emission predominant in nonpolar solvents varies

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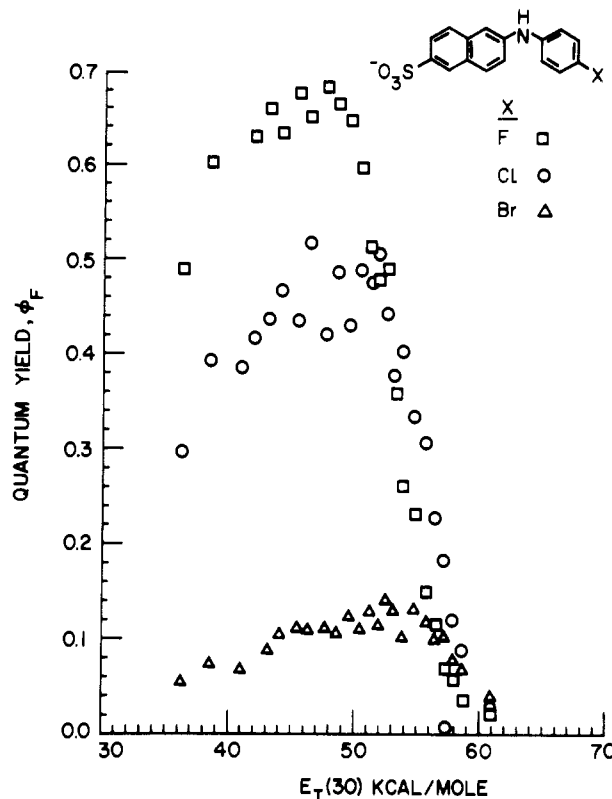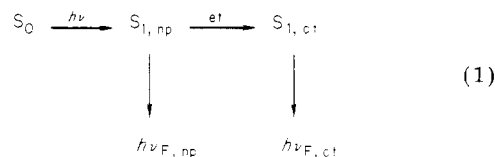

Figure 2. A plot of fluorescence quantum yields (ϕ_F) for 6-[(4-halophenyl)amino]-2-naphthalenesulfonates vs. $E_T(30)$ in a series of dioxane–water mixtures. The symbols refer to the 4-fluoro (□), the 4-chloro (○), and the 4-bromo (△) derivatives. The ϕ_F rises with increasing polarity in nonpolar solvents because the intersystem crossing rate decreases (the triplet yield is observed to fall). Although the intersystem crossing rate is influenced by the heavy-atom effect, solvent polarity does not further affect the pattern, and the typical ϕ_F decreases for the $S_{1,ct}$ states in polar solvents. (Reprinted from ref 13).

modestly with polarity and must be a locally excited state, labeled $S_{1,np}$. The second emission is quite sensitive to solvent polarity, the slope (0.65) being so large that only a charge-transfer fluorescence could be responsible. The state is labeled $S_{1,ct}$. The sequence of states is given in eq 1.

$$S_0 \xrightarrow{h\nu} S_{1,np} \xrightarrow{et} S_{1,ct}$$

$$\Big\downarrow \qquad\qquad \Big\downarrow \qquad\qquad (1)$$

$$h\nu_{F,np} \qquad h\nu_{F,ct}$$

The conclusion that two excited states ($S_{1,np}$ and $S_{1,ct}$) are involved in the photophysics of ANS derivatives may be tested in various ways. For example, the quantum yield of fluorescence (ϕ_F) shows two types of response to increasing solvent polarity: the ϕ_F for $S_{1,np}$ varies a little and ϕ_F for $S_{1,ct}$ drops dramatically. The quenching of ANS fluorescence in polar solvents is thus a property of the $S_{1,ct}$ state. The fluorescence quantum yield from the $S_{1,np}$ state (but not the influence of solvent polarity on ϕ_F) is diminished by intersystem crossing promoted by heavy atoms; ϕ_F for the $S_{1,ct}$ state is not affected by heavy atom substitution (Figure 2).

The two fluorescences respond differently to substituent changes. A common basis for comparing all substituent effects is established by extrapolating the E_F vs. $E_T(30)$ plots to hydrocarbon solvent ($E_T(30)$ =
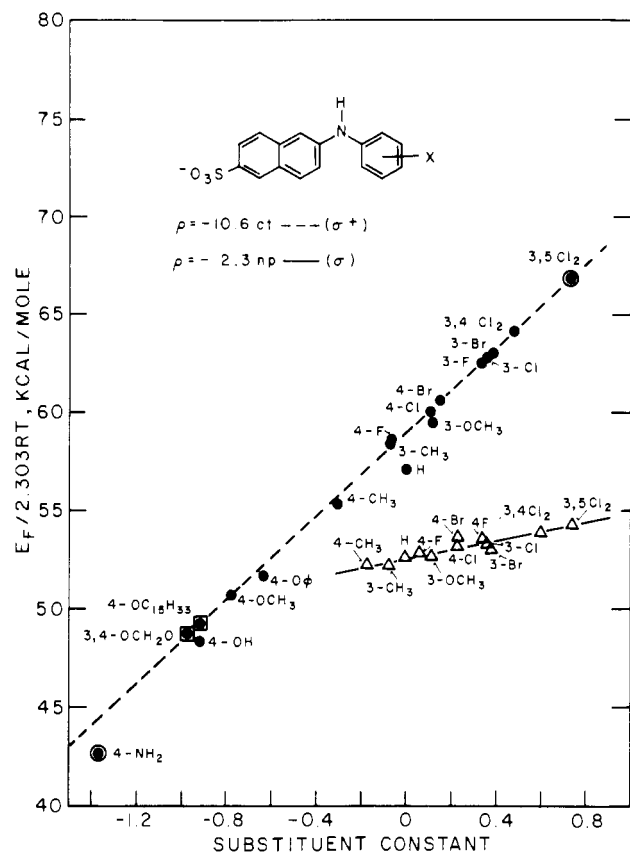
Figure 3. A plot of extrapolated fluorescence emission energies $(E_F)/2.303RT$ against σ (Hammett substituent constants) (low slope line, ρ –2.3) or σ^+ (Hammett–Brown substituent constants) (high slope line, ρ –10.6) for a series of 6-(phenylamino)-2-naphthalenesulfonates (2, X = substituents as noted). Points marked wth a circle were obtained from single measurements; points marked with a square were placed on the line to ascertain if the maxima corresponded to reasonable σ^+ constants. (Reprinted from ref 26, which should be consulted further details).

31), which yields the emission energies that would have been observed in the absence of solvation. Plots (Figure 3) of E_F against the Hammett σ ($S_{1,np}$ emission) or the Hammett–Brown σ^* substituent constants yield a ρ value, which characterizes the substituent sensitivity of the emission. The ρ value for the $S_{1,np}$ emission is relatively low, –2.3. The ρ value for the $S_{1,ct}$ emission is –10.6, so high that only a charge-transfer state could be responsible.

In contrast to the fluorescence maxima, the absorption maxima of 1 and 2 are not very sensitive to solvent or substituent changes (Table I), as expected for a transition, $S_0 \rightarrow S_{1,np}$, between two states of similar charge separation.

Other evidence in favor of the two-state interpretation of ANS photophysics comes from the effect of medium viscosity. The fluorescence of 2 in glycerol corresponds to an $S_{1,np}$ emission in spite of the high polarity of the solvent.[19] The high viscosity of glycerol inhibits the formation of the charge-transfer state. The correlation lines for $S_{1,np}$ emissions in nonpolar solvents allow a prediction of E_F in glycerol. Other viscous or rigid media permit only emission from the $S_{1,np}$ states. Thus, 2 emission in the anhydrous crystal,[20] or in pro-

tein binding sites[6] is $S_{1,np}$ due to restricted motion irrespective of the polarity of the site.

We have shown that alterations in the fluorescence spectra produced by substituent changes in 1 and 2 indicate different polarities for the same apomyoglobin binding site.[21] Although the strong fluorescence of the chymotrypsin-8,1-ANS complex in the crystal and in solution (λ_{max} 484 nm) might suggest an intermediate polarity binding site, Tulinsky and co-workers have shown by crystal structure studies that the binding site is quite polar with ionized groups on one side of the ANS and water on the other.[22] Fluorescent probes like 1 or 2 are not reliable indicators of the polarity of a protein binding site, notwithstanding the large number of studies using the technique.

The 8,1-ANS derivatives (1) yield fluorescence spectra that vary with solvent and substitution in a way similar to the variations found for the 6,2-ANS derivatives. The solvent sensitivities for both absorption and fluorescence spectra resemble those for 2, but the substituent sensitivity is somewhat larger (ρ –14).

(Methylphenylamino)naphthalenesulfonates (3 and 4) yield solvent-sensitive fluorescence maxima. The
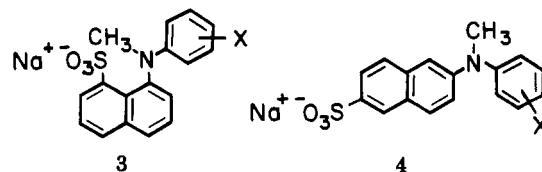
substituent effect for 4 turns out to be one the largest ever found experimentally (ρ ca. –25), and implies structural differences between the $S_{1,ct}$ states of 2 and 4 (see below).

Pressure changes on solutions of 9-[4-(dimethylamino)phenyl]anthracene and 8,1-ANS (1, X = H) change the ratio between two different fluorescence emissions, lending strong support to the "sequential two-state" interpretation for the photophysical behavior of ANS.[23]

Structure of S_0, $S_{1,np}$, and $S_{1,ct}$ States. We may now try to interpret the fluorescence results with the aid of other kinds of information in terms of structures for the various states. The small effect of N-phenyl substituent changes on ANS absorption spectra, crystal structure studies,[20] a theoretical analysis of the conformations of 2,[24] and consideration of models suggest that the phenyl group is neither coplanar with nor conjugated to the naphthalene ring in the S_0 state.

The $S_{1,np}$ state produced from the S_0 state by light absorption must initially have the same geometry. The modest respone of the $S_{1,np}$ fluorescence to substituent change in the N-phenyl group (ρ –2.3) shows that interaction in the excited state between the phenyl group and the excited moiety is not large. Thus, the N-phenyl group must be noncoplanar with the naphthalene ring; we shall take the angle between the ring planes to be 90° in the absence of crystal constraints.

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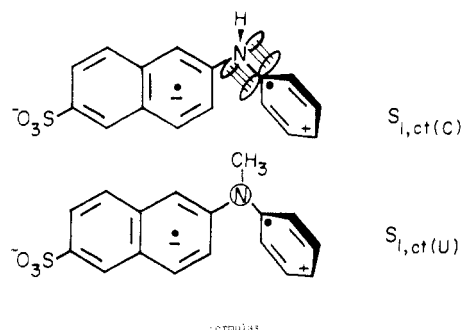(20) Camerman, A.; Jensen, L. H. *J. Am. Chem. Soc.* 1970, *92*, 4200–4203.

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Figure 4. Structures assigned to the charge-transfer states arising from **2** (X = H) ($S_{1,ct(C)}$ or **4** (X = H) ($S_{1,ct(U)}$), based on the ρ values which correlate the extrapolated emission energies. (Reprinted from ref 26).

The $S_{1,ct}$ state formed from **2** (hydrogen on nitrogen) responds to substituents with a ρ value of -10.6. A similarly high value (-9.1) is estimated for the stabilization of the α-cumyl carbonium ion (measured: -4.54 for solvolysis of α-cumyl chloride in 90% acetone–water,[25] with multiplication by two for equilibrium state substituent effects on the basis of "half-expressed" transition-state substituent effects). We may infer that the nitrogen is conjugated to the phenyl substituent in the $S_{1,ct}$ state of **2** (and **1**) just as the carbonium ion is conjugated to the ring in the solvolysis reaction.

The $S_{1,ct}$ state produced from **4** (methyl on nitrogen) is much more sensitive to substituent change in the N-phenyl group, with a ρ value of -25. Less delocalization of the positive charge in the phenyl ring would allow greater interaction with the substituent; in the $S_{1,ct}$ of **4**, the nitrogen is conjugated to the naphthalene and not to the N-phenyl group.[26]

The probable structures of the two different $S_{1,ct}$ states are shown in Figure 4. The states are designated C (conjugated) or U (unconjugated) depending on the relationship of the p orbital on nitrogen to the substituted phenyl ring. libration of the rings is no doubt required for passage to the transition state for electron transfer, either in formation or in loss of the charge-transfer state.

Dynamic Behavior of Excited States. The $S_{1,ct}$ state is clearly identified as the origin of the solvent-sensitive behavior of ANS derivatives. However, this information did not lead to a mechanism for the quenching of fluorescence. We considered the possibility that intersystem crossing was the pathway for quenching. In collaboration with Professor Michael Ottolenghi and his student, Naomi Orbach, we looked for the formation of triplets after nanosecond pulse excitation of **2** derivatives as a function of solvent polarity. Even for a bromo derivative (**2**, 4-X = Br), the concentration of triplet molecules decreased with increasing solvent polarity (Figure 5). Intersystem crossing is thus not responsible for the fluorescence quenching. Heavy-atom derivatives of ANS did not exhibit particularly enhanced fluorescence quenching in polar solvents.[27] Since no other state could be detected in the flash experiments (a low yield of solvated electron was formed in polar solvents (see below)) and since photochemical decomposition of **2** was quite in-

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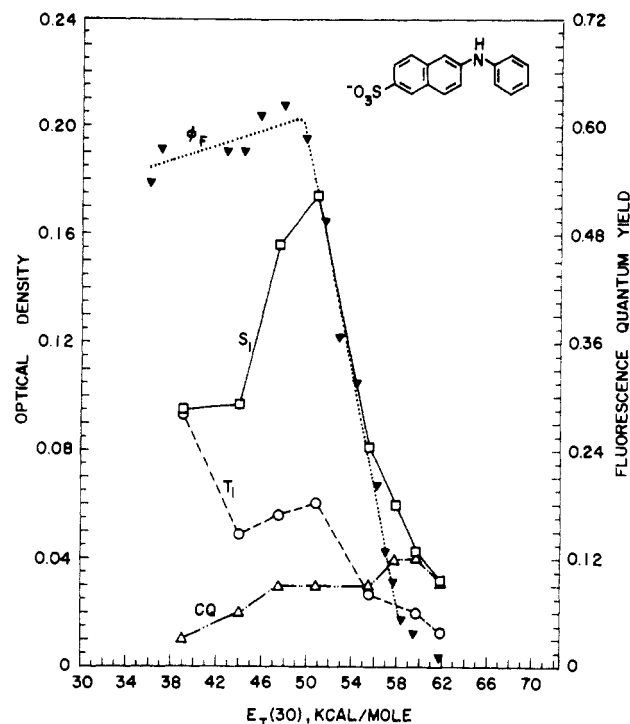

Figure 5. Plots of optical densities for light absorption of the excited states produced by nanosecond pulse excitation of 6-(phenylamino)-2-naphthalenesulfonate (**2**, X = H). ϕ_F for the dioxane–water mixtures are included. The shortest lifetime absorption under these conditions is assigned to $S_{1,np}$ or $S_{1,ct}$ states. The longest lived species is T_1. The solvated electron (CQ) has an intermediate lifetime. Its concentration increases smoothly but not markedly with increasing solvent polarity; the quenching of ANS fluorescence does not parallel the changes in e^- concentration with solvent polarity. (Reprinted from ref 13).

efficient, the $S_{1,ct}$ must return to the ground state, S_0.

We recognized that the $S_{1,ct}$ state could disappear (a) radiatively (charge-transfer emission) or (b) nonradiatively (electron transfer) (eq 2). Both processes led to

$$S_0 \xleftarrow{h\nu} S_{1,ct} \xrightarrow{et} S_0 \qquad (2)$$
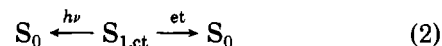
the ground state, S_0. It was not obvious how increased solvent polarity could favor the nonradiative (quenching) process over the radiative process for the same change in charge separation. We therefore measured the rates of both processes using the quantum yields of fluorescence and the fluorescence lifetimes (by single photon counting) as a function of solvent polarity for a number of ANS derivatives.

The radiative (k_r) and nonradiative (k_{nr}) rate constants are derived using eq 3–5. The radiative rates

$$\phi_F = k_r/(k_r + k_{nr}) \qquad (3)$$

$$k_r = \phi_F/\tau \qquad (4)$$

$$k_{nr} = (1 - \phi_F)/\tau \qquad (5)$$

are mildly sensitive to solvent polarity. The nonradiative rates are quite sensitive to solvent polarity. A plot of transition-state free energies for the nonradiative loss of S_1 gives linear correlations with $E_T(30)$, the two different slopes representing the disappearance of $S_{1,np}$ (low slope) or the $S_{1,ct}$ states.

Although the correlations certainly showed regularity, their meaning was obscure. I noted that there was some convergence of the lines, and also remembered the extrapolation of the Y vs. Z plots for organic solvent–water
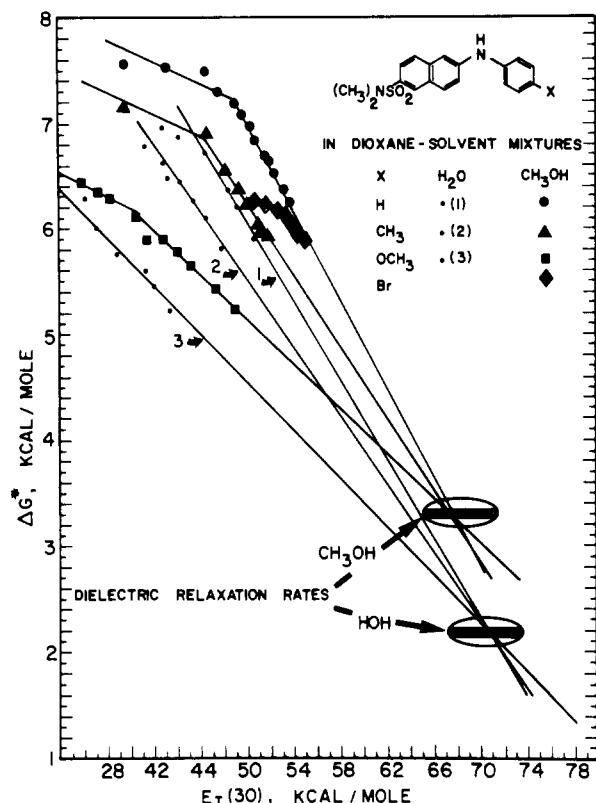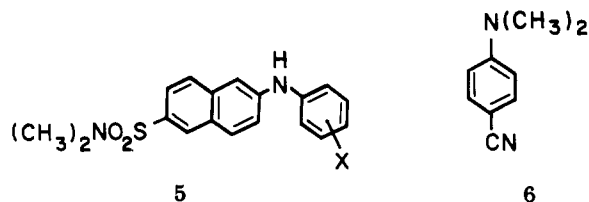
Figure 6. Plots of transition-state free energies (in kcal/mol) corresponding to the nonradiative rate constants (k_{nr}) for the decay of the excited states of N,N-dimethyl-(phenylamino)-2-naphthalenesulfonamides (5, 4-X = H, CH_3, CH_3O) vs. $E_T(30)$ in dioxane–water and dioxane–methanol mixtures. The correlation lines for different compounds extended to "common" regions, at approximately the dielectric relaxation rates for water (dioxane–water mixtures) or methanol (dioxane–methanol mixtures). The fluorescence emissions for 5 (4-X = Br) are "mixed"; a correlation line has not been drawn. The points for the most polar solvents give a line which extrapolates to the same "common region" as the lines for the other ANS derivatives.

mixtures. Lines for three different mixtures converged at the proper Y value, yielding a Z value for water.[15] I then extrapolated the correlation lines for ΔG^*_{nr} vs. $E_T(30)$ and found that the lines converged in a common region (Figure 6). The ΔG^* value for the common region corresponded roughly to the dielectric relaxation rate for water, suggesting that the process which controlled the nonradiative rate was the dielectric relaxation of the solvent! The divergence between the solvent effects on the radiative and nonradiative processes became understandable. The radiative rate was controlled largely by intramolecular factors; the nonradiative rate was controlled mostly by extramolecular factors.[28]

Would the conclusion about the importance of dielectric relaxation in water be true for other solvents? We decided to examine dioxane–methanol solutions of suitable ANS derivatives with the hope of extrapolating ΔG^*_{nr} vs. $E_T(30)$ correlation lines to the relaxation rate for pure methanol. The usual ANS derivatives, 2 or 4, exhibited $S_{1,ct}$ emission only in the most polar dioxane–methanol mixtures. We prepared a new series of compounds, the N,N-dimethyl-6-(phenylamino)-2-naphthalenesulfonamides (5) Fluorescence measure-

ments for the amides (5) showed two fluorescent states and substituent effects that were large for the $S_{1,ct}$ states and small for the $S_{1,np}$ states.[29] From fluorescence lifetime data and quantum yields, the ΔG^*_{nr} values were obtained and plotted against $E_T(30)$, yielding correlation lines which extrapolated to the dielectric relaxation time for methanol (Figure 6).[30]

The quenching of ANS fluorescence results from the promotion of the nonradiative electron-transfer by polar solvents. The dielectric relaxation time of the solvent is the major factor that affects the nonradiative electron-transfer rate: the more polar the solvent, the higher the electron-transfer rate.

Intramolecular Electron Transfer Rates and Mechanism. The two-state sequence is established for the excited states of 6,2-ANS derivatives. Restricting solvent motion (by increasing the viscosity or increasing the pressure) lowers the rate of formation of the $S_{1,ct}$ state to a level below that of the radiative rate for the $S_{1,np}$ state. In other words, emission occurs from the first excited state ($S_{1,np}$) rather than from the charge-transfer state. One might then be able to measure the rate of conversion of the $S_{1,np}$ state to the $S_{1,ct}$ or, in other words, measure the rate for the intramolecular electron-transfer process.

Huppert and Rentzepis[31] have shown that a series of linear alkanols are particularly useful as solvents for measuring the rates of formation and loss of the excited states of 4-(dimethylamino)benzonitrile (6). After the discovery of the dual fluorescence of 6 by Lippert and co-workers,[32] much effort by the group of Grabowski identified a "twisted charge-transfer state" (TICT) as the origin of the long-wavelength fluorescence of 6.[33,34] In fact, the two fluorescent states of 6 are completely analogous to those of 1-5.

The new derivatives prepared for the dioxane–methanol studies, e.g., TNSDMA (5, 4-X = CH_3), are particularly suitable for the study of fluorescence emission in organic solvents of intermediate polarity. We have found that the intramolecular electron-transfer process ($S_{1,np} \rightarrow S_{1,ct}$) can be observed after a 10-ps flash. The *rate of disappearance* of the $S_{1,np}$ state of TNSDMA is similar to the *rate of formation* of the intramolecular charge-transfer state, $S_{1,ct}$, of TNSDMA.[35]

Both rates decrease with increasing solvent viscosity; the rate constants parallel but are 6–10 times greater

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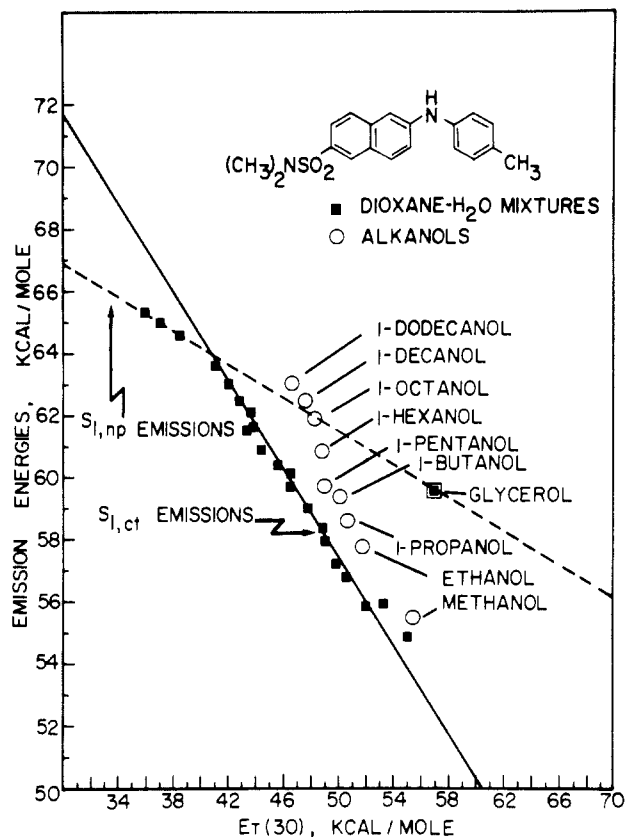
Figure 7. A plot of the emission energies, E_F, for N,N-dimethyl-6-[(4-methylphenyl)amino]-2-naphthalenesulfonamide (TNSDMA) in dioxane–water mixtures and in linear alkanols vs. $E_T(30)$. The low slope line (- -) correlates $S_{1,np}$ state emissions; the high slope line (—) correlates the $S_{1,ct}$ state emission. The correlation line for $S_{1,np}$ emission extrapolates to the observed E_F for glycerol. The average emission maximum in the higher, more viscous alkanols includes a contribution from $S_{1,np}$ emission (note how close the emission energies are to the correlation line extended to glycerol). The emission maximum in more polar, less viscous alkanols comes closer and closer with decreasing chain length to the value expected for an $S_{1,ct}$ emission. Steady-state fluorescence measurements reflect the major contributions to the emission spectrum and can be easily understood in terms of the correlations obtained in dioxane–water. The change in the ratio of the contributions of the two emissions with pressure has been thoroughly documented (A.M., H.G.): ref 23. Reprinted with permission from: Huppert, D.; Kanety, H.; Kosower, E. M. *Chem. Phys. Lett.* 1981, *84*, 48–53. Copyright 1981, North–Holland.

than the "lowest" dielectric relaxation rates for the C_3–C_{12} linear alkanols.[36] The rates change with solvent more than the rotational relaxation rates for the OH dipole (listed in Table II as dielectric relaxation times, τ_2). Chase and Hunt[37] have found that electron solvation rates are close to the rates corresponding to τ_2. A somewhat more complex process, perhaps involving several rotational relaxations, must control the intramolecular electron-transfer process in 6,2-ANS derivatives and will be discussed in more detail elsewhere.[38]

The disappearance of the $S_{1,ct}$ state was also monitored. These are the clearest examples of intramolecular electron-transfer rate measurements yet reported. The results,[35] including those for diols, are summarized in Table II, along with the dielectric relaxation times.

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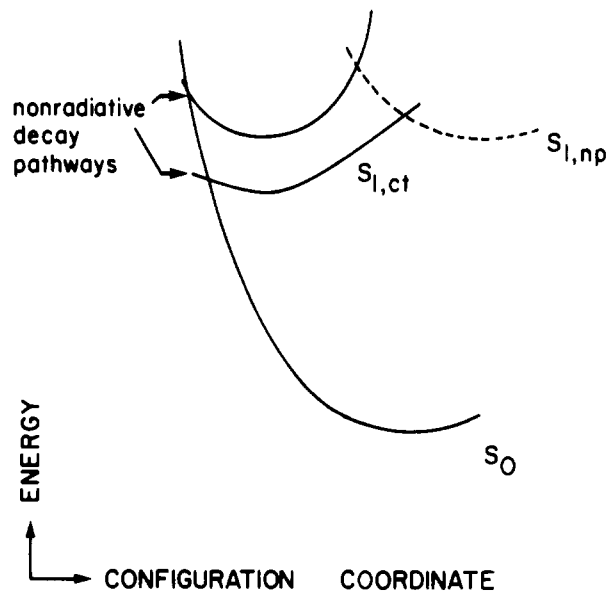

Figure 8. A free-energy diagram illustrating the relationships of the S_0, $S_{1,np}$, and $S_{1,ct}$ states. The charge-transfer state is shown in a minimally solvated state (charge-transfer emission competes with the $S_{1,np}$ emission) and in a state solvated by ca. 5 kcal/mol. The transition state for the nonradiative electron transfer decreases by ca. 7 kcal/mol. (Reprinted with permission from: Huppert, D.; Kanety, H.; Kosower, E. M. *Chem. Phys. Lett.* 1981, *84*, 48–53. Copyright 1981, North–Holland.

The rate of charge-transfer state formation is 20–30 times greater than the rate of its disappearance. The "Z value model"[15] (excited-state stabilization = ground-state destablization) is applied to the differences in emission energies for the $S_{1,np}$ and $S_{1,ct}$ states in the same solvent (Figure 7). The $S_{1,ct}$ stabilization energies (1.5–2.2 kcal/mol) are equivalent to the difference between the transition-state free energies (1.7–2.2 kcal/mol) for the formation and disappearance of the charge-transfer state in linear alkanols. The rate of formation of the $S_{1,ct}$ state is about 10 times faster in diols than expected from the stabilization energies. A free-energy vs. reaction coordinate diagram for the states is shown in Figure 8.

Other examples of the direct observation of the disappearance of an initially prepared excited state and the appearance of a charge-transfer state have been reported with 1-[4-(dimethylamino)phenyl]-3-(9-anthracenyl)propane by Eisenthal[39] and Mataga.[40,41]

Robinson[42,43] has proposed that spontaneous ionization of the initially formed S_1 state of 6,2-ANS occurs, a conclusion supported by Fleming,[44] who found e⁻ after pulse excitation of 8,1-ANS. However, biphotonic formation of a solvated electron is favored for 8,1-ANS,[45] acridine,[46] 2-naphtholate anion,[47] 2-naphthol,[48]

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(44) Sadkowski, P. J.; Fleming, G. R. *Chem. Phys.* 1980, *54*, 79–89.
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Table II
Decay (τ_d) and Rise (τ_r) Times of the $S_{1,np}{}^a$ and $S_{1,ct}$ States of
N,N-Dimethyl-6-[(4-methylphenyl)amino]naphthalene-2-sulfonamide[b] Compared with Dielectric Relaxation Times
(τ_1 and τ_2) for Linear Alkanols and Alkanediols

solvent	$E_T(30)$, kcal/mol[c]	n, cP[d]	τ_1, ps[e]	τ_2, ps[e]	$\tau_{d,np}$, ps[f]	$\tau_{r,ct}$, ps[f]	$\tau_{d,ct}$, ps[f]
methanol	55.5	0.547	68	g	<10	<15	400
ethanol	51.9	1.10	129	g	ca20	<30	1260
1-propanol	50.7	2.10	408	21	53	70	1940
1-butanol	50.2	2.79	625	26	81	90	2680
1-pentanol	49.1	3.61	851	27	95	109	3940
1-hexanol	48.8	4.93	1106	30	106	120	4750
1-octanol	48.3	8.23	1613	37	155	205	5300
1-decanol	47.6		1831	45	292	316	6410
1-dodecanol	46.7		2230[h]		400	i	7380
1,2-ethanediol	56.3				59	45	358
1,3-propanediol	54.9				97	85	602
1,2-propanediol	54.0				100	105	860

[a] Rise time for this state is pulse limited (ca. 10 ps). [b] At 23 ± 0.5 °C. [c] Solvent polarity parameter, from the charge-transfer absorption maximum of a pyridinium betaine (cf. Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Weinheim, 1979; linear with absorption maximum of 1-ethyl-4-carbomethoxypyridinium iodide (cf.: Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253). [d] Viscosity in centipoises; interpolation between literature values was used to obtain the values listed; 23 ± 0.5 °C. [e] Dielectric relaxation times for 23 °C: of the three obtained for linear alkanols, the two lowest are given. The longest is usually ascribed to the breaking of a hydrogen bond, followed by reorientation of the molecule. The longer the chain attached to the OH group, the slower the reorientation (cf.: Böttcher, C. F.; Bordewijk, P. "Theory of Electric Polarization"; Elsevier: Amsterdam, 1978; Vol. II). [f] ±10%. [g] Methanol and ethanol (times for 23 °C are estimated from reported data for somewhat different temperatures) exhibit one relaxation. Saxton, J. A.; Bond, R. A.; Coats, G. T.; Dickinson, R. M. *J. Chem. Phys.* **1962**, *37*, 2132. [h] Estimated from data at 40 °C; alcohol mp 22 °C. [i] Not measured.

and pyrene.[49] The photoionization of excited ANS systems must therefore be regarded as an interesting sidelight rather than a primary process. In fact, the species called "CQ" produced by nanosecond laser excitation of 6,2-ANS derivatives[13] is probably the solvated electron. The solvent effect on the production of this species is not parallel to the solvent effect on the formation or loss (quenching) of either the singlet or triplet states.

The conversion of the $S_{1,np}$ state to the $S_{1,ct}$ state is very fast and varies in a way parallel to but not identical with the dielectric relaxation times for the solvents, since the local environment around the excited molecule is not the same as that surrounding a solvent molecule. The experiments offer a way of attacking the problem of intramolecular electron transfer, which seems to be controlled in large part by the microenvironment of the excited molecule.

Solvent Effects on ρ Values. The fluorescence of the $S_{1,ct}$ state from 2 shows a high sensitivity to substituent, i.e., a high ρ value. The fluorescence from 4 shows a superhigh sensitivity. The values, as high as they are, are characteristic of charge-transfer processes in which the charge is delocalized only in the benzene ring.[50,51] Data for the substituent effects for both NH and NCH_3 compounds in dioxane–water solvents could be developed as plots of ρ values as a function of solvent polarity (Figure 9).

Conclusions

The ANS system is particularly adaptable to thorough studies of photophysical processes. At present, certain ANS derivatives offer the possibility of inves-
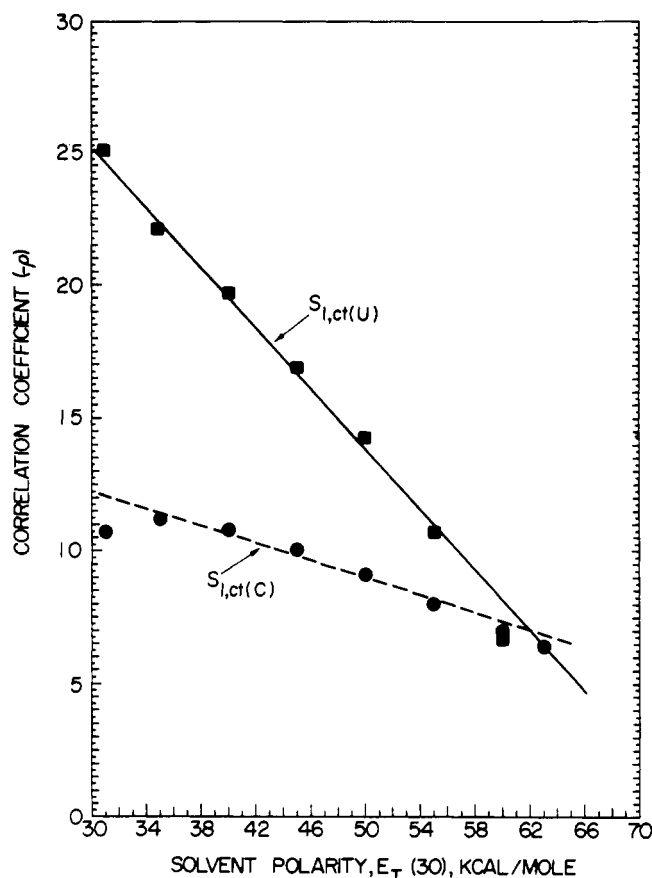
(46) Kellmann, A.; Tfibel, F. *Chem. Phys. Lett.* **1980**, *69*, 61–65.

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(51) See discussion and other references given in ref 26.

Figure 9. A plot of ρ values for $S_{1,ct(C)}$ (- - -) and $S_{1,ct(U)}$ (—) emissions vs. $E_T(30)$. The ρ values in various solvents correspond fairly well to those observed for other systems in various solvents. (Reprinted from ref 26).

tigating the mechanism of intramolecular electron transfer in detail. Intramolecular electron-transfer processes are controlled to a large extent by the dielectric relaxation processes of the solvent surrounding the molecule. The solvent effect on the Hammett "reaction constant" (ρ) is greater the greater the con-

centration of charge; the effects are particularly apparent in less polar solvents.

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Additions and Corrections

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Nai Zheng Huang and Franz Sondheimer: The Planar Dehydro[8]annulenes.

Page 96. In the second paragraph, line 18 should read: In the [4n + 2]annulenes, the outer protons are at low field (deshielded) and the inner protons at high field (shielded),.......