Scheme I

$$AA(S_0) \longrightarrow AA^* \tag{5}$$

$$AA^* \rightsquigarrow AA^3(n,\pi^*) \tag{6}$$

$$AA^3(n,\pi^*) + AA(S_0) \xrightarrow{k_7} \text{polymer} \tag{7}$$

$$AA^3(n,\pi^*) \overset{k_8}{\rightsquigarrow} AA(S_0)^\dagger \tag{8}$$

$$AA(S_0)^\dagger + M \xrightarrow{k_9} AA(S_0) + M \tag{9}$$

$$AA(S_0)^\dagger \xrightarrow{k_{10}} C_2H_4 + CO_2 \tag{10}$$

indicate that $I_{CGF}/I_0 \gtrsim 0.90$ for both carboxylic acids (249- *or* 193-nm excitation). This is at variance with our experimental results. Thus, the two-step decarboxylation mechanism proposed here, while not a unique explanation, is consistent with the observed energy disposal dynamics.

A comparison of our findings with observations on the solution-phase photochemistry of acrylic and methacrylic acid may provide some insight regarding the photophysical processes leading to product formation. Since polymerization, rather than decarboxylation, is observed in solution, it is likely that, following irradiation of, e.g., acrylic acid, a relatively long-lived excited state is formed. Studies of the UV-visible absorption spectroscopy of acrylic acid[15] indicate that excitation near 193 nm initially populates a $^1(\pi,\pi^*)$ state while 249-nm excitation initially populates a $^1(n,\pi^*)$ state [absorption at 308 nm corresponds to the low-energy tail of this (n,π^*) transition]. We suggest that regardless of the excited state initially populated, the $^3(n,\pi^*)$ is formed via rapid intersystem crossing. Such nonradiative processes can be particularly efficient in polyatomic molecules with low-frequency, e.g., torsional, degrees of freedom.[16] In solution, this triplet state may encounter ground-state acrylic acid and thereby initiate polymerization. The observation that acrylic acid polymerization can be triplet sensitized[17] is consistent with this hypothesis. If the $^3(n,\pi^*)$ state undergoes nonradiative decay to the ground state prior to encountering any ground-state acid, it can be rapidly relaxed by collisions with the solvent. As a result of this rapid vibrational relaxation, acrylic acid molecules which return to the ground state are left with insufficient internal energy to undergo unimolecular decarboxylation. In the gas phase, at the relatively low pressures characteristic of our experiments, the time between collisions involving two carboxylic acid molecules is $\gtrsim 10^{-5}$ s. Thus a significant fraction of electronically excited acid molecules may return to the ground state prior to such collisions. In this way, vibrationally hot ground-state molecules are formed which can undergo unimolecular decay in competition with collisional relaxation. The observation that the gas-phase pyrolysis of acrylic acids results in decarboxylation[2] appears consistent with this model. However, decarboxylation was found to occur in competition with other fragmentation channels, suggesting that heterogeneous processes may have been significant in the reported study.[2] The scenario suggested here is outlined in Scheme I, where AA represents acrylic acid and S_0, the ground electronic state; an asterisk indicates electronic excitation, a dagger (†) vibrational excitation, and M a collision partner, e.g., solvent or buffer gas molecules. An analogous scheme can be constructed in the case of methacrylic acid. In summary, we suggest that in solution, $k_7 \gtrsim k_8$ and $k_9 >> k_{10}$, whereas in the gas phase, $k_8 > k_7$ and $k_{10} \gtrsim k_9$. This scheme provides a relatively simple explanation for the fact that different photoproducts are observed following the UV irradiation of acrylic and methacrylic acid in gas and solution phases.

Conclusions

We find that both acrylic and methacrylic acid photofragment upon irradiation at 249 or 193 nm, forming CO_2 as a primary product. Vibrational excitation in the CO_2 fragment is monitored by infrared fluorescence and its extent is consistent with a statistical model for energy partitioning in unimolecular decompositions, assuming a fragmentation mechanism where CO_2 is formed in concert with a carbene. This suggests a novel approach for the generation of carbenes in the gas phase. Finally, we suggest a scheme which accounts for the apparently dichotomous reactivity of acrylic acid (and its derivatives) in the gas and solution phases.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The excimer laser used here was obtained with funds provided by a major instrumentation grant from the National Science Foundation (CHE 81-14966).

Registry No. Acrylic acid, 79-10-7; methacrylic acid, 79-41-4.

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Intramolecular Donor-Acceptor Systems. 10. Multiple Fluorescences from 8-(Phenylamino)-1-naphthalenesulfonates

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Abstract: 8-(Phenylamino)-1-naphthalenesulfonates (**1**) exhibit variations in fluorescence maxima and quantum yields with solvent polarity and substituent change. These facts suggest sequential formation of two excited states, a naphthalene-excited $S_{1,np}$ state and a charge-transfer state, $S_{1,ct}$, as in the case of the 6-(phenylamino)-2-naphthalenesulfonates (**2**) (cf. Kosower, E. M. *Acc. Chem. Res.* **1982**, *15*, 259). An inefficient photochemical dissociation of the sulfonate group to form 1-(phenylamino)naphthalene is reported. Previously reported excited-state kinetics are consistent with the two-step mechanism.

Introduction

The sensitivity of the fluorescence maxima and quantum yields of 8-(phenylamino)-1-naphthalenesulfonates (8,1-ANS, **1**) and 6-(phenylamino)-2-naphthalenesulfonates (6,2-ANS, **2**) was first recognized by Weber and Laurence.[2] In water, **1** and **2** are almost nonfluorescent but in nonpolar organic solvents, or when bound to proteins,[3-7] exhibit a strong fluorescence and a blue shift of the

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[1] (a) Tel-Aviv University. (b) State University of New York.

(2) Weber, G.; Laurence, D. J. R. *Biochem. J.* **1954**, *56*, xxxi.

(3) Turner, D. C.; Brand, L. *Biochemistry* **1968**, *7*, 3381.

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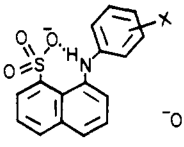

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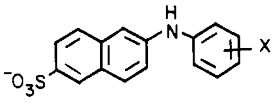

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fluorescence maximum as compared with that in water.

Kosower and co-workers[8-15] have elucidated the photophysical pathways for 6,2-ANS derivatives (**2**). Absorption of light leads to a naphthalene-excited state, $S_{1,np}$, for which the fluorescence maxima and quantum yields vary little with solvent and substituent change. The initially formed excited state is then transformed into a charge-transfer state, $S_{1,ct}$, for which the fluorescence maxima and quantum yields vary greatly with solvent and substituent change. The photophysical transformations are summarized in eq 1. The radiative rate for the $S_{1,ct}$ state decreases

$$\begin{tikzcd} S_{0,np} \arrow[r] & S_{1,np} \arrow[r, shift left] \arrow[d] & S_{1,ct} \arrow[l, shift left] \arrow[r] \arrow[d] & S_{0,np} \\ & h\nu_{F,np} & h\nu_{F,ct} & \end{tikzcd} \tag{1}$$

slightly with increasing solvent polarity but the nonradiative decay, via intramolecular electron transfer, increases greatly in rate.[11] Thus, the fluorescence of ANS derivatives is quenched in polar solvents. Of especial importance is the direct observation of the sequential formation of the two excited states by picosecond pulse techniques.[13]

We now show that the photophysical pathways for 8,1-ANS are similar to those for the 6,2-ANS (i.e., sequential formation of two excited states) even though certain structural features are quite different (an internal hydrogen bond, found in 8,1-ANS by X-ray crystallography[16-18] and NMR studies[19a]).

Results

The variation in the absorption and emission spectra of 8,1-ANS derivatives arising from changes in solvent polarity or substituents are reported in the following sections.

Absorption Spectra. The absorption maxima for 8,1-ANS derivatives (**1**) are summarized in Table I. In dioxane, four bands are apparent with maxima (ϵ in M^{-1} cm^{-1}) at 220 nm (43 000), 270 (16 000), 355 (6000) (sh), and 375 (7000). Changes in substitution on the *N*-phenyl group have little effect on the position of the longest wavelength absorption band, or the relative intensity of the two lowest energy transitions $[I(S_1)/I(S_2)]$. The longest wavelength maxima for compounds with electron-donating substituents are found at longer wavelengths than that for the unsubstituted **1**: 362 nm (X = 3-CF_3), 375 (X = H), 384 (X = 4-OCH_3). Correlating the absorption energies corresponding to the longest wavelength maxima with Hammett substituent constants yields a ρ value of −4.3.

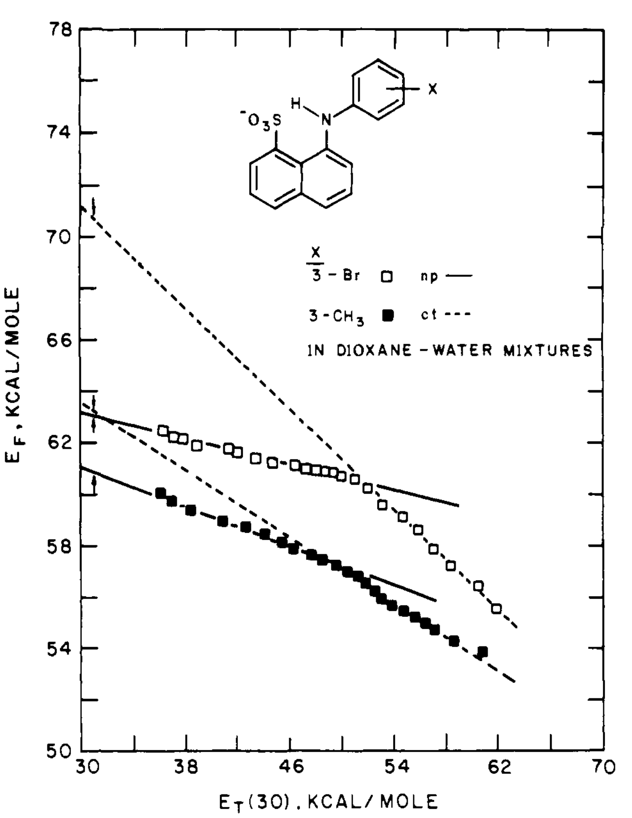
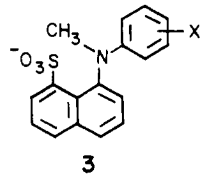


Figure 1. A plot of emission energies (in kcal/mol) vs. the solvent polarity parameter, $E_T(30)$ (in kcal/mol), for two 8-(phenylamino)-1-naphthalenesulfonates (**1**, X = 3-**Br**, 3-CH_3) in a series of dioxane–water mixtures. The solid line (—) correlates emissions assigned to the $S_{1,np}$ state and the dashed line (- - -) emissions from the $S_{1,ct}$ state. The arrows indicate the value of the expected emission energies in cyclohexane, $E_T(30)$ = 31.0.

Compounds with an N–CH_3 (**3**) rather than an NH group show a slight blue shift of the longest wavelength absorption band, 369 nm (ϵ 2000) for **3**, X = H, vs. 375 nm (ϵ 6000) for **1**, X = H, although the spectra are similar.



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The positions of the absorption maxima change little with changes in solvent (Table I). In water, the absorption spectra are broadened; the two long-wavelength bands merge into a single broad flat-topped absorption band, with the 375-nm band as a shoulder on the 352-nm band (ϵ 6500). The same spectroscopic changes are observed for N–CH_3 derivatives (Table I).

Emission Spectra. Fluorescence maxima and quantum yields for 8,1-ANS derivatives (**1**) in dioxane–water and ethanediol–water mixtures are given in Tables II, III, and IV, and for *N*-methyl-8,1-ANS derivatives (**3**) in Table V.[19b]

Solvent Polarity Effects. The emission energies (derived from the fluorescence maxima) for two derivatives of **1** in a series of dioxane–water mixtures are plotted against the $E_T(30)$ value (Figure 1). The reasons for correlating the fluorescence parameters with $E_T(30)$, an empirical solvent polarity parameter, have been thoroughly explained elsewhere.[8,20] Two correlation

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(19) (a) Penzer, G. R. *Eur. J. Biochem.* **1972**, *25*, 218. (b) Table III (8,1-ANS, **1**, X = 3-CF_3, 4-F, 3-CH_3, 3,5-$(CH_3)_2$, 4-OC_6H_5 in dioxane–water), Table IV (8,1-ANS, **1**, X = 3-Br, 3-Cl, 3-CF_3, 3-CH_3, 4-CH_3, 4-F, 3-OCH_3, 4-H in 1,2-ethanediol–water), and Table V (*N*-Me-8,1-ANS, **3**, X = H, 3,5-$(CH_3)_2$ in dioxane–water) are available as Supplementary Material. See note at end of paper.

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Table I. Solvent and Substituent Effects on the Two Longest Wavelength Absorption Bands of 8-(Phenylamino)-1-naphthalenesulfonates

ANS (1) deriv X =	solvent	$E_T(30)^a$	$\lambda_{max}(1)^b$	$\lambda_{max}(2)^c$	Int R^d
H	dioxane	36.0	375	355 sh	1.17
	ethanol	51.9	375	355 sh	1.14
	1,2-ethanediol	56.3	376	355 sh	1.16
	HOH	63.0	375 sh	352	0.90
4-CH$_3$	dioxane	36.0	381	355 sh	1.10
	ethanol	51.9	378	355 sh	1.07
	1,2-ethanediol	56.3	380	355 sh	1.13
	HOH	63.0	375 sh	352	0.97
4-OCH$_3$	dioxane	36.0	384	358	0.94
	ethanol	51.9	380	355	0.94
	1,2-ethanediol	56.3	384	358	1.07
	HOH	63.0	375 sh	349	0.92
3-Cl	dioxane	36.0	365	350 sh	1.14
	ethanol	51.9	366	350 sh	1.14
	1,2-ethanediol	56.3	365	350 sh	1.11
	HOH	63.0	br band	(352 nm)	
NCH$_3$ (3)					
H	dioxane	36.0	369	345	1.16
	HOH	63.0	br band	(355 nm)	

[a] Solvent polarity parameters based on the absorption maxima for pyridinium phenol betaine 30. (Reichardt, C.; Dimroth, K. *Justus Liebigs Ann. Chem.* 1963, *661*, 1). [b] Longest wavelength absorption band maximum. [c] Second longest wavelength absorption band maximum. [d] Ratio of the intensities of the $\lambda_{max}(1)$ to $\lambda_{max}(2)$.

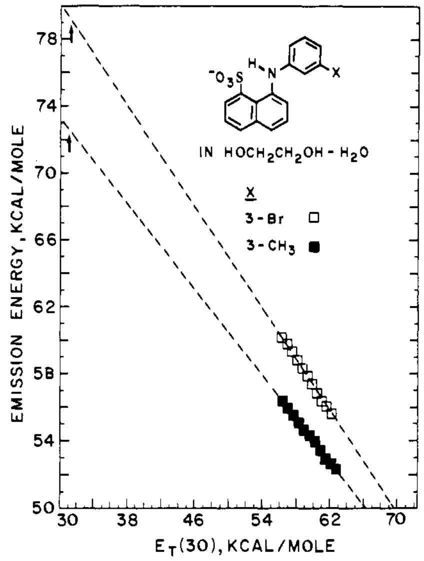

Figure 2. A plot of emission energies (in kcal/mol) vs. the solvent polarity parameter, $E_T(30)$ (in kcal/mol), for two 8-(phenylamino)-1-naphthalenesulfonates (**1**, X = 3-**Br**, 3-CH$_3$) in a series of 1,2-ethanediol mixtures.

lines show two different types of behavior. Emission energies for derivatives of **1** in a series of 1,2-ethanediol–water mixtures show a good correlation with a high slope vs. $E_T(30)$ (Figure 2).

The quantum yields of fluorescence vary with solvent polarity in a way which is much more sensitive to the solvent polarity than the emission energies. In the nonpolar range, the quantum yield is usually high. At a solvent polarity value which varies with the particular ANS derivative, the quantum yield begins to drop rapidly; the yield is so low in solvents as polar as water that it is difficult to measure accurately. To illustrate the parallel behavior of both emission energy and quantum yield, data for the 3-bromo and 3-chloro derivatives (**1**, X = Cl, 3-Br) are plotted in Figure 3.

Effect of Solvent Viscosity. The emissions of 8,1-ANS derivatives in two solvents with similar polarities but different viscosities, 1,2-ethanediol ($E_T(30)$ = 56.3, η 20.9 cP (20 °C[21a])) and glycerol ($E_T(30)$ = 57.0, η 1412 cP (20 °C[21b])), are compared in Table VI. For many of the 8,1-ANS derivatives (especially those with electron-donating substituents), the maxima are at shorter wavelengths in glycerol than in 1,2-ethanediol and the quantum yields are higher.

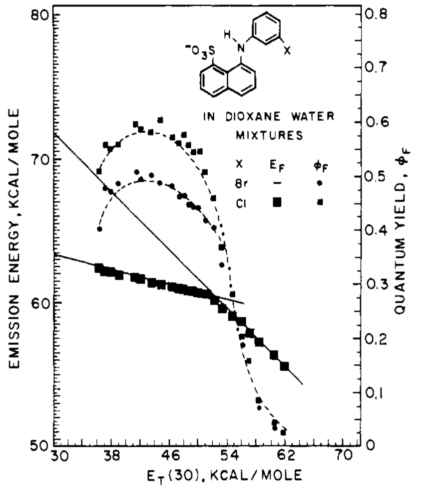

Figure 3. A plot of fluorescence quantum yields for two 8-[(3-halophenyl)amino]-1-naphthalenesulfonates (**1**, X = 3-Cl, 3-Br) vs. the solvent polarity parameter, $E_T(30)$, in a series of dioxane–water mixtures. Emission energies for the chloro derivatives are also shown.

Changes due to Substituents on the *N*-Phenyl Group. The two types of fluorescence respond differently to substituent changes. In order to have a common basis for comparison of the data for differently substituted compounds, the correlation lines (E_F vs. $E_T(30)$) are extrapolated to hydrocarbon solvents ($E_T(30)$ = 31), yielding the emission energies that would have been observed in the absence of solvation. The results from 1,2-ethanediol–water solutions extrapolate to uniformly higher values than those from dioxane–water solutions, but the extrapolated emission energies are correlated by the same ρ values as noted in the Discussion. (Note the arrows indicating these values in Figures 1 and 2.)

***N*-Methyl Derivatives.** (Methylphenylamino)naphthalenesulfonates (**3**) display solvent-sensitive fluorescence spectra. The parallel behavior of the emission energies and quantum yields for 8,1-ANS (**1**) and *N*-methyl-8,1-ANS (**3**) are illustrated for **1**, X = 3,5-(CH$_3$)$_2$, and **3**, X = 3,5-(CH$_3$)$_2$, vs. $E_T(30)$ in Figure 4. The two-slope behavior is seen for **3** as well as for **1**.

Naphthalene Ring Substituent Changes. A derivative with a methoxysulfonyl group (SO$_3$CH$_3$) (**4**, X = 3,5-(CH$_3$)$_2$) was prepared through exhaustive methylation of the corresponding **3** derivative.

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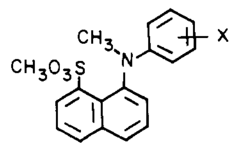

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Absorption and emission data for **4** in various solvents are given in Table VII. Fluorescence emission was strong enough to be observed only in nonpolar solvents. Emission energies correlate with $E_T(30)$ values with a slope of 0.8.

Heavy-Atom Effects. Emission from the $S_{1,np}$ state of halogenated 6,2-ANS derivatives (**2**, X = 3-Cl, 3-Br, 4-Cl, 4-F, 4-Br) is decreased markedly by an intramolecular heavy-atom effect,[8,15] whereas the emission from the $S_{1,ct}$ state was apparently unaffected. The quantum yield and its variation with solvent polarity is hardly affected by the heavy-atom substituent in two 8,1-ANS derivatives (**1**, X = 3-Cl, 3-Br) (Figure 2).

Phosphorescence Spectra. 8,1-ANS derivatives in EPA (ether:pentane:ethanol, 5:5:2) glass at 77 K exhibit a barely detectable phosphorescence, $\phi_P/\phi_F \ll 0.01$. Data are listed in Table VIII.

Fluorescence Lifetimes. The decay of the excited states of 8,1-ANS (**1**, X = H) was measured using the single photon counting technique. The lifetimes and fluorescence quantum yields [τ (ns), ϕ_F] are as follows: CH_3OH [5.7, 0.21], 80% CH_3OH:H_2O [3.3, 0.07], 50% CH_3OH:H_2O [1.2, 0.02], $HOCH_2CH_2OH$ [4.1, 0.15], glycerol [3.8, 0.12]. Lifetimes for **1** (X = H) in dioxane-water mixtures have been reported previously.[11] The derived nonradiative constants are included in Table IX.

Photochemistry. Irradiation of 8,1-ANS (1, X = H) in Methanol. After long irradiation, a slight decrease in the emission of **1** (X = H) was observed, accompanied by a new feature in the excitation spectra at 338 nm. The photochemical quantum yield was estimated to be $<10^{-2}$. After 2 weeks of irradiation of **1** (X = H) in methanol, most of the compound was recovered along with a small amount of a new compound with a higher mobility on TLC. Elution with $CHCl_3$ from an alumina column gave a pure sample of the photoproduct [λ_{max} (dioxane): 338 nm (abs), 408 (emiss), 428 (emiss, CH_3OH)], identified as 1-(phenylamino)naphthalene (**5**), by ^1H NMR, comparison chromatography (TLC), UV, and fluorescence spectra.

Discussion

The central feature of the photophysics of 8-(phenylamino)-1-naphthalenesulfonate is that there are two fluorescent states which differ in response to solvent and substituent change. Plots of both fluorescence emission energies (E_F) (Figure 1) and the quantum yields (ϕ_F) (Figure 3) vs. a solvent polarity parameter, $E_T(30)$, show good correlation lines but with two different slopes. That there are two lines correlating emission energies for **1** and **3** suggests that the fluorescences arise from two different excited states. The position of the emission predominant in nonpolar solvents varies modestly with polarity and is a naphthalene-excited state, labeled $S_{1,np}$. The great sensitivity of the second emission to solvent polarity (Figures 1–3) can be explained only by a charge-transfer fluorescence. The state is labeled $S_{1,ct}$. The two-state mechanism is illustrated with molecular formulas in Figure 5.

A plot of extrapolated emission energies divided by $2.303RT$ (for proper scaling in the comparison) vs. Hammett substituent constants yields a ρ of −4.8 for the $S_{1,np}$ emission and −14.1 for the $S_{1,ct}$ emission (Figure 6). The corresponding ρ values for 6,2-ANS are −2.6 and −10.6, respectively.[8] A ρ value of −14.6 is obtained for the extrapolated emission energies for ethanediol–water mixtures, identical with the ρ value obtained for dioxane–water mixtures. High slopes for correlations with ρ^+ are characteristic of emissions from a charge-transfer state. Strong electron-attracting groups on the naphthalene ring such as SO_3CH_3 ($\sigma > 0.85$),[21c] favor emission from the charge-transfer state even more than sulfonate groups (SO_3^-, σ 0.09). Comparison of 6,2-ANS[8] and 8,1-ANS (Tables II and III) indicates that the shift from $S_{1,np}$ to $S_{1,ct}$ emission for a given substituent on the N-phenyl group occurs for **1** at a lower solvent polarity. The internal hydrogen bond probably increases the effective electron-attracting ability of the sulfonate group (σ (SO_3H) 0.45, (SO_3^-) 0.09). With data for only two N-Me 8,1-ANS derivatives (**3**, X = H, 3,5-$(CH_3)_2$), a ρ value, desired for comparison with the high ρ value found for the charge-transfer emissions of the N-Me-6,2-ANS derivatives,[10] was not obtained.

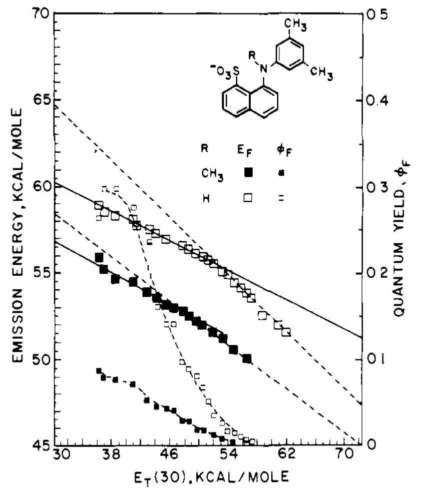

Figure 4. A plot of emission energies and quantum yields for 8-[(3,5-dimethylphenyl)amino]-1-naphthalenesulfonate and for 8-[methyl(3,5-dimethylphenyl)amino]-1-naphthalenesulfonate, vs. the solvent polarity parameter, $E_T(30)$, in a series of dioxane–water mixtures.

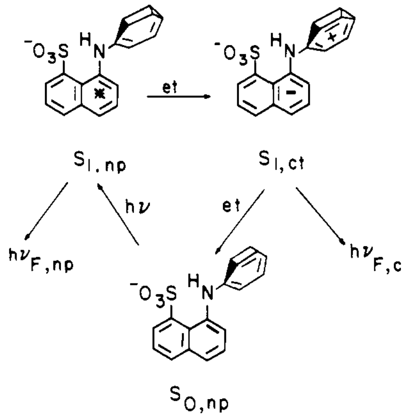

Figure 5. Formulas illustrating the geometric relationships of the phenyl and naphthalene rings of 8-(phenylamino)-1-naphthalenesulfonate (**1**) in a sequence of photophysical conversions initiated by the absorption of light by the ground state, $S_{0,np}$. The initially formed excited state, $S_{1,np}$, undergoes an intramolecular electron-transfer reaction to form the charge-transfer state, $S_{1,ct}$. The latter returns to the ground state via another electron-transfer process. The symbols used are: et, electron transfer; $h\nu_a$, excitation energy: $h\nu_{F,np}$, fluorescence emission from the $S_{1,np}$ state; $h\nu_{F,ct}$, fluorescence emission from the $S_{1,ct}$ state. The phenyl ring is noncoplanar with the naphthalene ring.

The small effect of N-phenyl substituent changes on ANS absorption spectra, crystal structure studies, and consideration of models suggest that the N-phenyl group is not coplanar with the naphthalene ring. The ground state may therefore be designated as $S_{0,np}$ (np = nonplanar, indicating the plane of the N-phenyl group is not parallel to the plane of the naphthalene ring) and the electronic transition corresponding to the longest wavelength absorption, $S_{0,np} \rightarrow S_{1,np}$. The assignments are parallel to those for 6,2-ANS derivatives.[8]

The modest variation of the $S_{1,np}$ state fluorescence with substituent change on the N-phenyl group shows that interaction with the naphthalene ring in the excited state is not large. In fact, it is about what might be expected for variation with substitution on an aniline, with $\rho = 4$ for $XC_6H_4NH_3^+$ dissociation in ethanol, in comparison with ρ of −4.3 for absorption and −4.8 for emission. The corresponding ρ values for 6,2-ANS derivatives are −3.6 and

Table II. Emission Data for 8-(Phenylamino)-1-naphthalenesulfonates in Dioxane–Water Mixtures[a,b]

solvent, % diox[c]	$E_T(30)$[d]	λ_{max}[e] (ϕ_F),[f] phenyl substituent, X =					
		H	4-Cl	3-Br	3-Cl	4-CH_3	4-OCH_3
99.9	36.4	471 (0.52)	473 (0.44)	456 (0.40)	455 (0.51)	488 (0.29)	528 (0.020)
99.6	37.2	472 (0.52)	473 (0.49)	460 (0.48)	459 (0.56)	490 (0.28)	529 (0.018)
99.3	37.9	474 (0.51)	474 (0.47)	460 (0.47)	460 (0.55)	492 (0.27)	531 (0.015)
98.9	39.0	475 (0.50)	475 (0.48)	462 (0.49)	461 (0.56)	494 (0.24)	531 (0.015)
98.3	40.6					496 (0.23)	532 (0.012)
98.0	41.4	478 (0.45)	476 (0.48)	463 (0.51)	463 (0.60)	498 (0.20)	533 (0.011)
97.1	42.1	480 (0.43)	478 (0.46)	464 (0.49)	464 (0.59)	500 (0.19)	534 (0.008)
96.1	42.8	481 (0.42)				503 (0.17)	535 (0.007)
95.2	43.5	482 (0.38)	479 (0.41)	466 (0.50)	466 (0.58)	504 (0.15)	537 (0.006)
93.6	44.8	483 (0.36)	480 (0.41)	467 (0.49)	467 (0.61)	507 (0.12)	
92.5	45.6	484 (0.30)					
90.5	46.5	486 (0.28)	481 (0.37)	468 (0.48)	467 (0.57)	510 (0.12)	
87.4	47.4	487 (0.24)	482 (0.35)	469 (0.46)	468 (0.56)		
84.3	48.1	488 (0.20)	482 (0.33)	469 (0.46)	469 (0.58)	514 (0.10)	
81.1	48.8	489 (0.19)		470 (0.45)	470 (0.56)		
78.0	49.4	490 (0.16)	483 (0.29)	470 (0.44)	471 (0.55)	517 (0.08)	
74.9	50.0	491 (0.15)	484 (0.27)	471 (0.44)	472 (0.55)		
71.8	50.6	493 (0.12)	486 (0.26)			520 (0.07)	
68.6	51.1	495 (0.11)	488 (0.23)	472 (0.42)	473 (0.51)		
62.4	52.1	497 (0.08)	490 (0.18)	475 (0.41)	475 (0.46)	523 (0.05)	
53.0	53.2	501 (0.05)	493 (0.13)	480 (0.34)	477 (0.37)	527 (0.04)	
43.6	54.8	506 (0.02)	495 (0.08)	484 (0.24)	480 (0.28)	530 (0.03)	
37.4	56.0	510 (0.01)	498 (0.05)	488 (0.19)	484 (0.20)		
31.1	57.0	514 (0.008)	504 (0.04)	494 (0.16)	490 (0.16)		
21.8	58.4	520 (0.006)	512 (0.02)	500 (0.08)	497 (0.09)	535 (0.02)	
12.4	60.5	525 (0.004)	522 (0.01)	507 (0.04)	505 (0.05)	537 (0.01)	
6.1	61.9	530 (0.003)	530 (0.01)	514 (0.03)	512 (0.03)		

[a] At 25 ± 2 °C. Temperature has a minor influence on the position or intensity of the fluorescence maximum in this temperature range. [b] For details of the measurement and the instrumentation, see the Experimental Section. [c] Percentage of dioxane by volume mixed with water. [d] Values are from Table 2, p 28, in Reichardt, C.; Dimroth, K. *Fortschr. Chem. Forsch.* 1968, *11*. 1, or derived by linear interpolation. [e] In nm. [f] ±10%. Referred to quinine sulfate in 0.1 N H_2SO_4, $\phi_F = 0.55$, not corrected for refractive index.

Table VI. Fluorescence Data for 8-(Phenylamino)-1-naphthalenesulfonates (1) in 1,2-Ethanediol[a] and Glycerol[b]

8,1-ANS, 1, X =	1,2-ethanediol		glycerol	
	λ_{max}, nm[c]	ϕ_F[d]	λ_{max}, nm[c]	ϕ_F[d]
3-CF_3	466	0.45	472	0.30
3-Br	475	0.45	481	0.29
3-Cl	474	0.48	481	0.24
4-Cl	492	0.19	492	0.20
3-OCH_3	505	0.04	494	0.09
H	502	0.15	496	0.11
4-F	506	0.05	502	0.05
3-CH_3	507	0.06	506	0.14
3,5-$(CH_3)_2$	517	0.04	512	0.08
4-CH_3	523	0.01	513	0.03
4-OCH_3	550	0.002	526	0.02
4-OPh	540	0.004	515	0.02

[a] $E_T(30) = 56.3$ (ref 8). Viscosity, 20.9 cP (20 °C) (ref 21a, p 312). [b] $E_T(30) = 57.0$ (ref 8). Viscosity, 1412 cP (20 °C) (ref 21b, p 202). [c] ±2 nm. [d] ±10%, corrected for solvent refractive index.

Table VII. Absorption and Emission Data for 1-Methoxysulfonyl-8-[methyl(3,5-dimethylphenyl)amino]naphthalene in Various Solvents

solvent	$E_T(30)$	λ_{max}[b]		ϕ_F[c]
		absorption	emission	
hexane	30.9	390	544	0.027
cyclohexane	31.2	388	546	0.038
CCl_4	32.5	390	564	0.028
benzene	34.0	386	580	0.010
dioxane	36.0	385	590	0.005

[a] Reichardt, C. "Solvent Effects in Organic Chemistry"; Verlag Chemie: Weinheim, 1979. [b] ±2 nm. [c] ±10% values referred to quinine sulfate in 0.1 N H_2SO_4, $\phi_F = 0.55$.

Table VIII. Emission Data for 8-[(X-Phenyl)amino]-1-naphthalenesulfonate Derivatives in Ether:Pentane:Ethanol (5:5:2) Glasses at 77 K[a]

substituent X	λ_{max}, nm[b]		ϕ_P/ϕ_F[c]
	fluorescence	phosphorescence	
H	436	500, 565, 610	<0.01
4-Cl	432	500, 555, 590	<0.01
3-Cl	423	500 sh, 555, 590 sh	<0.01
4-OCH_3	466	510, 580, 620	<0.01
3-Br	423	510 sh, 555, 590 sh	<0.01

[a] Solutions were purged with N_2 before freezing. [b] ±2 nm. Maxima not corrected. [c] Peak height ratio, using excitation at 370 nm.

–2.6.[8] The excitation is therefore localized n the naphthalene ring. Some conjugation between the amino group and the phenyl ring is plausible for one of the conformers.

Since there are two different noncoplanar conformers in crystals,[16–18] it is likely that noncoplanar conformers are present in solution. Thus, a coplanar conformation of the two rings is not essential to fluorescence as has been suggested by Penzer,[19] based on NMR studies.

The similarity of the absorption spectra of 8,1-ANS derivatives to the spectra of other 1-substituted naphthalenes (NH_2, OH, CN, CHO)[22,23] further indicates that the naphthalene ring is the locus of the two lowest energy electronic transitions.

N-Me-8,1-ANS derivatives show the same changes as N–H derivatives in absorption spectra on transfer from organic solvents to water. Therefore, the absorption spectra are not influenced by solvent-induced changes in intramolecular hydrogen bonding. (Cody and Hazel[16–18] have shown that in both conformers of 8,1-ANS, an intramolecular hydrogen bond is present between the N–H and the sulfonate group.) Moreover, the great similarity in position, extinction coefficient, and sensitivity to solvent change of the absorption spectra of 8,1-ANS and 7,1-ANS derivatives[3]

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(23) Suzuki, S.; Fujii, T.; Ishikawa, T. *J. Mol. Spectrosc.* **1975**, *57*, 490.

Table IX. Rate Constants for Decay of Excited States of 8-(Phenylamino)-1-naphthalenesulfonate

solvent	Z^a (kcal/mol)	log k_{nr}[b] (log k)[c]	log k[d]	log k_{nr}[e,f]
HOH	94.6-95	9.60 (9.60)	9.70	
DOD		9.11 (9.12)	9.30	
CH_3OH:HOH(1:1)	90.9			8.92[e]
$HOCH_2CH_2OH$:HOH(2:1)			8.54	
$DOCD_2CD_2OD$:DOD(2:1)			8.29	
CH_3CH_2OH:HOH(1:1)	89.2[g]	8.69 (8.71)		
CH_3OH:HOH(4:1)	87.3			8.46[e]
$HOCH_2CH(OH)CH_2OH$	87.2[h]	8.23 (8.32)		8.36[e]
$HOCH_2CH_2OH$	85.1	8.18 (8.28)	8.28	8.32[e]
$DOCD_2CD_2OH$			7.96	
CH_3OH	83.6	8.11 (8.23)	8.08	8.15[e]
CH_3OD		7.90 (8.05)	7.79	
CD_3OH			8.05	
CD_3OD			7.77	
CH_3CH_2OH	79.6	7.86 (8.08)	7.90	
CH_3CH_2OD		7.72 (8.00)	7.69	
$CH_3CH_2CH_2OH$	78.3		7.84	
$(CH_3)_2NCHO$	68.5	7.46 (7.98)		
20.2% dioxane:HOH (DW)	91.4			9.06[f]
29.6 DW	89.9			8.89[f]
38.9 DW	88.6			8.81[f]
43.6 DW	87.9			8.76[f]
48.3 DW	87.0			8.57[f]
57.7 DW	85.5			8.41[f]
61.5 DW	84.7			8.39[f]
67.1 DW	83.5			8.26[f]
74.9 DW	81.5			8.12[f]
84.3 DW	78.5			8.00[f]
90.5 DW	76.6			7.86[f]

[a] Reference 26. [b] k_{nr}, nonradiative rate constants (ref 25). [c] $k = k_{nr} + k_r$, radiative rate constants (ref 25). [d] k, nonradiative + radiative rate constants (ref 24). [e] k_{nr}, nonradiative rate constants (Kosower, E. M.; Kanety, H., this study). [f] k_{nr}, nonradiative rate constants (ref 11). [g] Derived from the Y value (1.655) for 50% ethanol-water (Grunwald, E. Winstein, S. *J. Am. Chem. Soc.* 1948, *70*, 846) via the relationship, $Y = 0.35338Z - 29.946$ (ref 26). [h] Derived from the $E_T(30)$ value (57.0) for glycerol (Kosower, E. M.; Dodiuk, H. *J. Am. Chem. Soc.* 1974, *96*. 6195-6187) and $Z = 1.4 E_T(30) + 7.39$ (Professor C. Reichardt, personal communication).

(in which there is no intramolecular hydrogen bond) imply that intramolecular hydrogen bonding in 8,1-ANS (**1**) does not affect the energy difference between the ground state and the two lowest singlet states.

Fluorescence Quenching. From the plots of quantum yield and emission energies vs. the solvent polarity parameter, it is clear that the quenching of ANS fluorescence in polar solvents is a property of the $S_{1,ct}$ state. The quenching process has been identified for 6,2-ANS derivatives as an intramolecular electron transfer, converting $S_{1,ct}$ into $S_{0,np}$.[8]

Effect of Solvent Viscosity. The rate of conversion of the $S_{1,np}$ state to $S_{1,ct}$ state is lowered in the viscous solvent, glycerol, for 6,2-ANS (**2**);[8] emission from 8,1-ANS (**1**) in glycerol is mainly from $S_{1,np}$ (for **1**, in the series from X = 4-OC_6H_5 to 3-CH_3 in Table VI) or from both $S_{1,np}$ and $S_{1,ct}$ states (for **1**, in the series from X = 3-CH_3 to 4-F in Table VI). The assignments are based on the relative positions of the emission maxima and the magnitudes of the quantum yields in glycerol and 1,2-ethanediol. Shorter wavelength maxima and higher ϕ_F are characteristic of $S_{1,np}$ emission. Lifetime measurements on **1** (X = H) in both solvents yield very similar k_r (1,2-ethanediol, 3.7 × 10^7 s^{-1}; glycerol, 3.2 × 10^7 s^{-1}) and k_{nr} (ethanediol, 2.1 × 10^8 s^{-1}; glycerol, 2.3 × 10^8 s^{-1}).

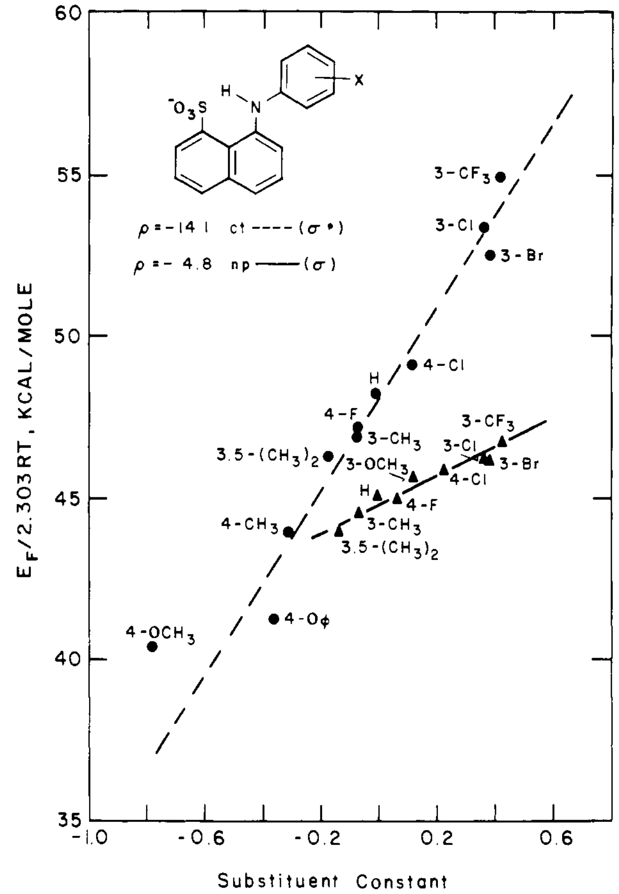

Figure 6. A plot of emission energies (in kcal/mol) of 8,1-ANS derivatives for cyclohexane ($E_T(30)$ = 31) vs. the substituent constants (σ or σ+). The energies were obtained for both $S_{1,np}$ and $S_{1,ct}$ emissions by the extrapolations shown in Figure 1. The energies were divided by 2.303*RT* in order to scale them appropriately for correlation with Hammett substituent constants which are based on equilibrium constants.

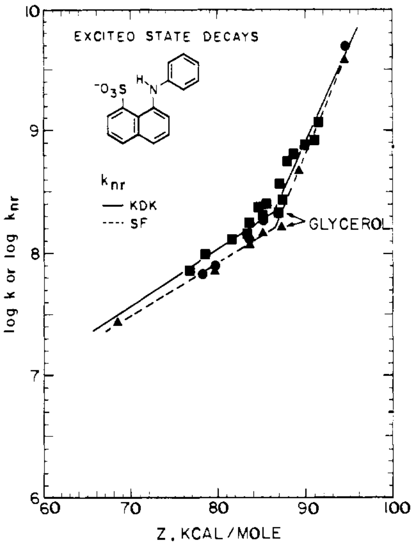

Figure 7. A plot of the log of the nonradiative decay constant (or the decay rate constant) for 8-(phenylamino)-1-naphthalenesulfonate (**1**, X = H) against the solvent polarity parameter, *Z* value.[26] A change in the slope in the intermediate polarity range is clearly visible for all three sets of data: k_{nr},[11] and k_{nr}.[25]

Further support for the two-state mechanism comes from fluorescence lifetime measurements for 8,1-ANS derivatives in solvents of different polarity.[11] The radiative rate constants (k_r) are mildly sensitive to solvent polarity. The nonradiative rates are quite sensitive to solvent polarity. Nonradiative rate constants, k_{nr}, for 8,1-ANS in a series of different solvents, reported recently by two groups,[24,25] are summarized together with our results[11] in Table IX.

The log k obtained by Nakamura and Tanaka (k(NT)),[24] the log k_{nr} obtained by Sadkowski and Fleming (k(SF)),[25] and the

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(25) Sadkowski, P. J.; Fleming, G. J. *Chem. Phys.* **1980**, *54*, 79.

log k_{nr} measured in our laboratories in dioxane–water and other solvent mixtures (k_{nr}(KDK))[11] for the decay of the excited states of 8,1-ANS (**1**) are plotted against the solvent polarity parameter, *Z* value[26] in Figure 7. The correlation lines exhibit a low slope in the low polarity solvent range and a high slope in the high polarity range. Two different excited states must thus be involved; the variation in the rate constants with solvent polarity parallels the change in the position of the fluorescence maximum and the quantum yield of fluorescence for 8,1-ANS.

Pressure changes on solutions of 8,1-ANS[27] (**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.

General Scheme for Excitation and Decay of 8,1-ANS Derivatives. The $S_{1,np}$ state can decay through at least four channels: (a) radiative, (b) internal conversion (ic), (c) intramolecular electron transfer, and (d) photochemical reaction. The ic channel accounts for no more than 30% of the decay, and the major decay channel is radiative in nonpolar solvents. In more polar solvents, the rate of the electron-transfer reaction which converts $S_{1,np}$ to $S_{1,ct}$ becomes greater than the radiative rate. The electron-transfer reaction could be reversible, as is the case for the corresponding states of the 6,2-ANS derivative, 6,2-TNSDMA.[14]

Intersystem Crossing. In contrast to 6,2-ANS derivatives,[8,15] intersystem crossing (isc) to the triplet accounts only for a minor part of the decay of the $S_{1,np}$ state in nonpolar solvents (small heavy-atom effect, barely detectable phosphorescence). It seems likely that a lower intersystem crossing rate is responsible for the failure to observe a triplet–triplet transition[28] and resistance to photochemical changes which proceed via a triplet state.

Seybold et al.[29] have not detected room-temperature phosphorescence from 8,1-ANS isomers and from 1-(phenylamino)naphthalene either at room temperature or in EPA at 77 K, and, therefore, intramolecular hydrogen bonding is not an essential feature leading to lack of phosphorescence. Fleming et al.[28] found no evidence for a triplet–triplet absorption spectrum for 8,1-ANS in ethanol and water, implying that isc is not a major decay route for the $S_{1,ct}$ state either.

The photochemical decay route (conversion of 8,1-ANS to 1-(phenylamino)naphthalene) is a minor pathway and has not been studied in detail. Grellman and Schmitt[30] have found that 1-(methylphenylamino)naphthalene is much more resistant to photochemical change than the corresponding 2-isomer.

The $S_{1,ct}$ state can decay through two channels. In solvents of intermediate polarity, the major decay route is radiative. In fluid solvents of high polarity, most of the $S_{1,ct}$ disappears through the intramolecular electron-transfer reaction leading to a vibrationally excited state of S_0.

Both the formation and the disappearance of the $S_{1,ct}$ state of TNSDMA (a 6,2-ANS derivative) have been studied using picosecond and nanosecond techniques at a single temperature in different solvents[13] and in 1-propanol at different temperatures.[14] Preliminary results[31] for the formation time of the $S_{1,ct}$ state of 8,1-ANS (**1**, X = H) (ethanediol, 73 ps; 1-propanol, 61 ps) and for **1**, X = 4-CH_3 (ethanol, 82 ps) are very similar to the rise times for the $S_{1,ct}$ and to the decay times for the $S_{1,np}$ states of 6,2-TNSDMA[13] and DMAB (4-(dimethylamino)benzonitrile)[32] in these solvents. DMAB exhibits dual fluorescences, which appear to arise from a two-state sequence similar to those reported for the ANS series. The reciprocal of the intramolecular electron-transfer rate constants measured for these compounds in different alcohols correlates extremely well with the constant charge dielectric relaxation times τ_1.[13,14,20,33] It thus appears that solvent motion controls the conversion of the $S_{1,np}$ state to the $S_{1,ct}$ state for 8,1-ANS as well as for 6,2-ANS.

Some published 8,1-ANS photophysical mechanisms are, in our view, obscure and do not explain all of the relevant facts. Sadkowski and Fleming[25] discussed the excited-state decay with the focus on thermal ionization of the initially formed excited state to a solvated electron[28] as the main quenching mechanism. The electron is ejected into a solvent trap produced somehow by the sulfonate group. Such a trap should be quite different for 6,2-ANS derivatives, but, as noted above, 8,1-ANS and 6,2-ANS derivatives (in fact, all ANS derivatives, regardless of substitution pattern) behave in a similar fashion. Further, solvated electron formation appears to be photoionization and *biphotonic*, as summarized elsewhere.[13,20] The well-defined solvent and substituent effects on the position of light emission are not explained, nor is the origin of two types of fluorescence made clear.

Nakamura and Tanaka have confirmed and extended the studies of Sadkowski and Fleming through an examination of the temperature effect on the decay kinetics of the excited states of 8,1-ANS.[34] However, the mechanism[24] included a "CTTS" state (following Sadkowski and Fleming) for which there is no independent evidence and which does not take into account the dual fluorescences exhibited by ANS derivatives. Without a correct assignment of species, a definitive interpretation of the rate constants and activation energies was not possible.

Conclusions

We have shown in this study that the two-state mechanism presented before for 6,2-ANS derivatives (**2**) applies also for 8,1-ANS derivatives (**1**). Some differences between the two systems are as follows: (a) the charge-transfer emission for 8,1-ANS is more sensitive to substituent change on the *N*-phenyl group; (b) for the same substituent on the *N*-phenyl group, the switch to charge-transfer emission occurs in a solvent of lower polarity for the 8,1-ANS system; (c) no heavy atom effect is observed in the 8,1-ANS system. An interesting photochemical reaction for 8,1-ANS has been observed.

Experimental Section

Materials. The synthesis of 8,1-ANS (**1**) derivatives was carried out by a modification of the Corey[35] method. A mixture of 8-amino-1-naphthalenesulfonic acid (AmNS) (5–10 mmol) and the appropriate aniline (15–30 mmol) was heated under nitrogen at 130–170 °C for 1–7 days. The loss of AmNS was followed by TLC on silica gel (methanol:benzene, 40:60). In no case was reaction carried to the point of complete disappearance of AmNS. After cooling, HCl (10–20%) was added, the precipitate filtered off and washed with chloroform to remove the aniline, and the product purified by crystallization or chromatography on silica, using benzene–methanol in various proportions as eluant. All compounds were dried for at least 2–3 days over P_2O_5 under vacuum. Specifics for the various derivatives follow.

8-[(3-(Trifluoromethyl)phenyl)amino]-1-naphthalenesulfonate (1, X = 3-CF_3): reaction, 7 days at 170 °C; purification, threefold chromatography on silica (elution: benzene–methanol), crystallization from water; yield 1%. ^{1}H NMR (Me_2SO-d_6) (ppm): NH, 10.70 (1 H, s), aromatic H, 6.8–8.3 (10 H, m).

8-[(3-Bromophenyl)amino]-1-naphthalenesulfonate (1, X = 3-Br): reaction, 6 days at 150 °C; purification, chromatography on silica (elution: benzene–methanol), crystallization from water; yield 2%. ^{1}H NMR (Me_2SO-d_6) (ppm): NH, 10.77 (1 H, s), aromatic H, 6.8–8.3 (10 H, m).

8-[(3-Chlorophenyl)amino]-1-naphthalenesulfonate (1, X = 3-Cl): same procedure as that used for **1**, X = 3-Br; yield, 1%. ^{1}H NMR (Me_2SO-d_6) (ppm): NH, 10.79 (1 H, s), aromatic H, 6.8–8.3 (10 H, m).

8-[(3,5-Dimethylphenyl)amino]-1-naphthalenesulfonate (1, X = 3,5-$(CH_3)_2$): reaction, 48 h at 160 °C; purification, chromatography on silica (elution: benzene–methanol), recrystallized three times from water; yield 15%. ^{1}H NMR (Me_2SO-d_6) (ppm): NH, 10.6 (1 H, s), aromatic H,

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6.8–8.3 (9 H, m), CH_3, 2.00 (6 H, s).

8-[(4-Methylphenyl)amino]-1-naphthalenesulfonate (1, X = 4-CH_3): same procedure as that used for 1, X = 3,5-$(CH_3)_2$; yield, 1%. ^1H NMR (Me_2SO-d_6) (ppm): NH, 10.56 (1 H, s), aromatic H, 7.0–8.3 (10 H, m), CH_3, 2.23 (3 H, s).

8-[(3-Methylphenyl)amino]-1-naphthalenesulfonate (1, X = 3-CH_3): reaction, 72 h at 160 °C; purification, chromatography on silica (elution: benzene–methanol), crystallized three times from water; yield 12%. ^1H NMR (in Me_2SO-d_6) (ppm): NH, 10.60 (1 H, s), aromatic H, 6.6–8.3 (10 H, m), CH_3, 2.24 (3 H, s).

8-[(4-Fluorophenyl)amino]-1-naphthalenesulfonate (1, X = 4-F): reaction, 24 h at 170°C. The yellow precipitate obtained after addition of HCl was recrystallized three times from water, yield 6%. ^1H NMR (Me_2SO-d_6) (ppm): NH, 9.3 (1 H, s), aromatic H, 7.1–8.3 (10 H, m).

8-[(4-Chlorophenyl)amino]-1-naphthalenesulfonate (1, X = 4-Cl): reaction, 72 h at 140 °C. The material which precipitated after addition of 10% HCl was freed from AmNS by dissolution in water. The product was isolated by evaporation of the filtrate and recrystallized from a small amount of water; yield 2.5%. ^1H NMR (Me_2SO-d_6) (ppm): NH, 10.73 (1 H, s), aromatic H, 7.1–8.3 (10 H, m).

8-[(4-Phenoxyphenyl)amino]-1-naphthalenesulfonate (1, X = 4-C_6H_5O): reaction, 48 h at 170 °C. After addition of 10% HCl, the mixture was extracted with chloroform, the $CHCl_3$ evaporated, and the residue chromatographed on silica (elution: benzene–methanol); the yellow product was crystallized three times from water, yield 18%. ^1H NMR (Me_2SO-d_6) (ppm): NH, 10.66 (1 H, s), aromatic H, 6.9–8.3 (15 H, m).

8-[(4-Methoxyphenyl)amino]-1-naphthalenesulfonate (1, X = 4-CH_3O): reaction 48 h at 150–160 °C. The precipitate obtained after treatment with 10% HCl was dissolved in aqueous $NaHSO_3$ (1.4 M):Na_2SO_3 (0.08 M). The solution was brought to pH 3.0 with HCl and the precipitate recrystallized from 10% NaOH, yield 10%. ^1H NMR (Me_2SO-d_6) (ppm): NH, 10.1 (1 H, s), aromatic H, 7.0–8.3 (10 H, m), 4-OCH_3, 3.72 (3 H, s).

8-(Phenylamino)-1-naphthalenesulfonate as the ammonium salt (1, X = H) was obtained from Merck. The purity of 8-(phenylamino)-1-naphthalenesulfonates was established by TLC on silica gel in two different solvent systems: benzene:methanol (60:40) and chloroform:methanol (60:40). The important spectroscopic properties are: IR (KBr) 3550–3350 (broad band), 1610, 1510, 1450, 1240, 1180, 1130, 1050, 840 cm^{-1}; UV (various solvents) four absorption bands at 375 nm (ϵ 6000–7000), 355 (sh) (5000–7000), 270 (16 000–18 000), and 220 (42 000–48 000).

8-(Methylphenylamino)-1-naphthalenesulfonate (3, X = H): prepared according to Corey et al.,[35] recrystallized from 10% NaOH. ^1H NMR (Me_2SO-d_6) (ppm): 6.2–8.6 (11 H, m), 2.9 (3 H, s). UV (dioxane) λ_{max} (ϵ_{max}): 365 nm (2100), 340 sh, 255 (16 000).

8-[Methyl(3,5-dimethylphenyl)amino]-1-methoxysulfonylnaphthalene (4). 8-[(3.5-Dimethylphenyl)amino]-1-naphthalenesulfonate (1, X = 3,5-$(CH_3)_2$) (0.25 g, 0.8 mmol) and 0.11 mL (1.2 mmol) of dimethyl sulfate in acetone (10 mL) were refluxed for 4 h. Sodium carbonate (0.2 g, anhydrous) and dimethyl sulfate (0.2 mL) were then added, and the mixture was refluxed for 20 h. The solvent was removed under vacuum, the residue extracted with chloroform, the solution dried (Na_2SO_4), and the solvent evaporated. The residue was chromatographed on silica (elution: chloroform), giving the product in 20% yield, mp 123 °C. ^1H NMR ($CDCl_3$) (ppm): 6.2–8.6 (9 H, m), 3.45 (3 H, s), 3.25 (3 H, s), 2.2 (6 H, s). UV (dioxane) λ_{max} (ϵ_{max}): 385 nm (1300), 285 (10 600), 255 (15 000).

8-[Methyl(3,5-dimethylphenyl)amino]-1-naphthalenesulfonate (3, X = 3,5-$(CH_3)_2$). 4 and 1 M KOH/CH_3OH were refluxed for 15 min; the solution was acidified with H_2SO_4/CH_3OH. The precipitate was filtered off, filtrate evaporated, and the residue recrystallized three times from water. ^1H NMR (Me_2SO-d_6) (ppm): 6.2–8.6 (9 H, m), 3.0 (3 H, s), 2.0 (6 H, s). UV (dioxane) (λ_{max} (ϵ_{max})): 365 nm (1950), 345 sh, 252 (14 000).

Spectroscopic Measurements. A Cary Model 17 spectrophotometer was used to measure absorption spectra. A Perkin-Elmer Hitachi MPF–4 spectrofluorimeter with a corrected spectra attachment and a digital integrator was used. Quinine sulfate in 0.1 N H_2SO_4 (ϕ_F = 0.55) was the reference standard for quantum yield measurements.

Fluorescence Lifetimes. Fluorescence decay times were measured by the single photon counting technique as described previously.[11] Solvents were obtained from Merck: dioxane was spectroscopic grade, 1,2-ethanediol "zur Analyse", and glycerol for fluorescence microscopy. The last was handled in a glove bag under dry nitrogen. Water was triple distilled.

Photochemistry. The ammonium salt of 8-(phenylamino)-1-naphthalenesulfonate (1, X = H) (0.15 g, 0.6 mmol) in methanol (100 mL, spectroscopic grade) was irradiated at 360 nm for 2 weeks in a Rayonet reactor. The solvent was evaporated and the residue chromatographed on alumina (elution: chloroform), yielding 14 mg (0.06 mmol) of 1-(phenylamino)naphthalene (5): UV (methanol) λ_{max} (ϵ_{max}) 338 nm (8700), 252 (17 500); fluorescence λ_{max} (ϕ_F) dioxane 408 nm (0.45), methanol 428 nm (0.22); ^1H NMR ($CDCl_3$) (ppm) 6.9–8.1 (11 H, m), 5.2 (1 H, br s).

Registry No. 1 (X = 3-CF_3), 86747-90-2; 1 (X = 3-Br), 67472-73-5; **1** (X = 3-Cl), 86747-91-3; **1** (X = 4-Cl), 86747-92-4; 1 (X = 3-OCH_3), 86747-93-5; **1** (X = H), 17966-20-0; **1** (X = 4-F), 86747-94-6; **1** (X = 3-CH_3), 86747-95-7; **1** (X = 3,5-$(CH_3)_2$), 86747-96-8; 1 (X = 4-CH_3), 86747-97-9; **1** (X = 4-OCH_3), 86747-98-0; **1** (X = OPh), 86747-99-1; 3 (X = H), 86748-00-7; 3 (X = 3,5-$(CH_3)_2$), 86748-01-8; **4** (X = 3,5-$CH_3)_2$), 86748-02-9.

Supplementary Material Available: Spectroscopic data in Tables III, IV, and V (3 pages). Ordering information is given on any current masthead page.

Aliphatic Hydroxylation Catalyzed by Iron Porphyrin Complexes

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Abstract: The hydroxylation of unactivated alkanes has been observed in a catalytic system containing iodosylbenzene and various iron porphyrins. The yields and distributions of products have been found to be sensitive to the peripheral substitution pattern of the porphyrin. The oxidation of cyclohexane with chloro(5,10,15,20-tetra-*o*-tolylporphyrinato)iron(III) [Fe(TTP)Cl] gave a 31% yield of cyclohexanol and 6% cyclohexanone based on iodosylbenzene. Two samples of Fe(TTP)ClCl with differing atropisomeric composition gave different product ratios. The hydroxylation of cycloheptane under these conditions and in the presence of bromotrichloromethane gave 24% cycloheptanol and 18% bromocycloheptane. Steric selectivity was observed by comparing the hydroxylation of *cis*-decalin with Fe(TPP)Cl, Fe(TTP)Cl, Fe(TNP)Cl, and Fe(TMP)Cl. The hydrogen-isotope effect for cyclohexane hydroxylation by Fe(TTP)Cl was found to be 12.9 ± 1. A mechanism for hydroxylation is proposed on the basis of these results that involves initial oxidation of the iron porphyrin, hydrogen atom abstraction from the alkane, and rapid collapse of this radical to give the product alcohol and to regenerate the iron(III) catalyst.

The heme-containing monooxygenase cytochrome P-450 is known to oxidize a wide variety of organic compounds.[1] Among the more biologically significant of these processes are O- and N-dealkylation, olefin and arene epoxidation, and steroid hy-

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