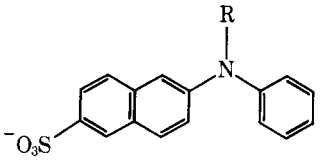
Multiple Fluorescences. 4. The Protonated Form of *N*-Alkyl-2-*N*-arylamino-6-naphthalenesulfonates

Hanna Dodiuk[1a] and Edward M. Kosower*[1a,b]

Contribution from the Department of Chemistry, Tel-Aviv University, Ramat-Aviv, Tel-Aviv, Israel, and the Department of Chemistry, State University of New York, Stony Brook, New York, 11794. *Received June 10, 1976*

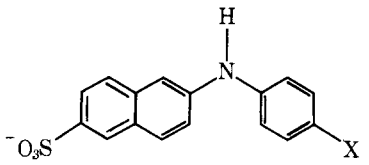
Abstract: The unusual fluorescence maximum (λ_{max} 405 nm; λ_{max} expected 468 nm) which can be observed from 2-*N*-alkyl-2-*N*-phenylaminonaphthalene-6-sulfonates (**1**) in glycerol at 25 °C is now identified as arising by way of a protonation reaction of a vibrationally excited state of **1**. The structure of the protonated product is shown by NMR to be the *N*-alkyl betaine (*N*-methyl in the case of **3M**) of 6-sulfonato-3β-tetralenone *N*-phenylimine (**3**). The high quantum yield of photoproduct (**3**), ϕ_H = 0.05, in glycerol at 25 °C, the stability of the product and its strong fluorescence (ϕ_F = 0.3) are responsible for the confusion about the fluorescence spectrum of **1M** in glycerol, in which the fluorescence of **3** can alter or cover the spectrum of **1** in the course of a usual measurement. With low exciting light intensities, the fluorescence spectrum of **1** in glycerol can be observed (λ_{max} 470 nm). The emissions are also readily distinguished by different excitation spectra. The protonated product can also be produced in 1,2-ethanediol and 1,2-propanediol via the quenching of charge-transfer states. Lack of wavelength dependence, temperature effect, or isotope effect on the quantum yield of the protonation reaction point to a fast proton transfer (estimated k, 1.1×10^8 s^{-1}). A complete scheme for the excited state behavior of 2,6-arylaminonaphthalenesulfonate derivatives is presented.

Seliskar and Brand[2a] reported a remarkable shift in the fluorescence emission maximum of *N*-methyl-2-phenylamino-6-naphthalenesulfonate (**1M**) in glycerol solution on warming from 300 K (λ_{max} 413 nm) to 320 K (λ_{max} 488 nm). The authors proposed that solvent relaxation around the excited state of **1** was incomplete at the lower temperature but



1

1M, R = CH_3
1E, R = CH_2CH_3
1HE, R = CH_2CH_2OH



2

became complete at a temperature 20 °C higher. Apart from the difficulties imposed by the high-temperature coefficient required for such a relaxation, our examination of the temperature dependence of the emission maximum of the compound lacking the *N*-methyl group (**2**) suggested that relaxation of the glycerol around the excited state of **2** (X = H) was probably complete below 0 °C.[2b] We therefore reexamined the emission of glycerol solutions of **1**.

A solution of pure *N*-methyl-ANS (**1M**) in dry glycerol exhibited an emission maximum at 405 nm which changed very little over the temperature range 283–337 K, using excitation at either 320 or 360 nm. The unusual asymmetric shape of the emission curve, as reported previously,[2a] was confirmed but the high-temperature sensitivity of the position of the maximum could not be reproduced in our initial experiments. However, after we had developed a clear understanding of the experimental system, the "shift" reported by Brand and Seliskar could be observed.

The behavior was so different from what we might have expected[3] on the basis of our work with ANS derivatives lacking the *N*-methyl group (**2**) that we carried out an investigation of the emission of **1M** and several closely related compounds in both viscous and fluid solvents.[4]

Results

N-Methyl-, *N*-ethyl-, and *N*-(2-hydroxyethyl)-2-*N*-phenylamino-6-naphthalenesulfonates (**1M, 1E,** and **1HE**) as sodium salts were prepared and their fluorescence parameters measured in a series of dioxane–water mixtures according to the procedure developed previously.[3] The excellent correlation of emission energies, E_F, derived from the fluorescence maxima and the solvent polarity parameter, $E_T(30)$,[4] is illustrated in Figure 1. The quantum yields of fluorescence (Figure 1) exhibit a pattern reasonably similar to those seen before for ANS derivatives: moderate change with solvent polarity in the nonpolar solvents and very sharp changes with solvent polarity in the polar solvents, which are explained elsewhere.[3b] Data are summarized in Table I.

As noted above, emission spectra for **1M** (and for **1E** and **1HE**) showed a maximum at 405 nm in glycerol. More important, the excitation spectrum for the 405-nm emission was strikingly different from that observed for **1M** in dioxane (Figure 2), suggesting that a chemical transformation had occurred. Yet, the absorption spectrum of a solution of **1M** in glycerol was apparently identical with that in dioxane both before and after its fluorescence had been measured, and only after we noted an absorption increase at 280 nm in one such post-fluorescence spectrum were we able to establish a photochemical process as the origin of the chemical change. In contrast, heating **1M** in glycerol under any conditions (even 3 h at 250 °C) produced none of the product found soon after exposure to light.

The photochemical transformations of **1M, 1E,** and **1HE** were effected in glycerol and the products isolated by careful evaporation of the solvent under high vacuum. Since no satisfactory method for further purification of the product was found, traces of glycerol remained and were useful as an internal reference in Fourier transform proton NMR. The photoproduct could also be prepared by irradiation in 1,2-ethanediol.

Exploratory experiments on irradiation of ANS derivatives (**2**, X = CH_3O, CH_3, H, and Cl) in glycerol containing sulfuric

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

Solvent % dioxane-water[c]	$E_T(30)$ value[d]	Alkyl (R =): λ_{max}[e] (ϕ_f)[f]		
		CH_3	CH_2CH_3	CH_2CH_2OH
99.9	36.3	425 (0.57)	429 (0.51)	426 (0.38)
99.6	37.0		430 (0.52)	428 (0.37)
99.1	38.5	426 (0.57)	432 (0.46)	430 (0.42)
98.1	41.1			432 (0.40)
97.2	42.0	430 (0.52)	435 (0.46)	
96.3	42.7			435 (0.41)
95.3	43.2	435 (0.51)	439 (0.43)	
94.4	44.2		440 (0.40)	438 (0.40)
92.5	45.6	440 (0.48)	442 (0.40)	440 (0.39)
90.6	46.5	443 (0.45)	446 (0.37)	442 (0.41)
85.9	47.8	446 (0.45)	450 (0.35)	444 (0.41)
81.3	48.7	448 (0.42)	453 (0.34)	445 (0.35)
76.6	49.7	450 (0.38)	455 (0.32)	448 (0.38)
71.9	50.5	452 (0.37)	457 (0.30)	452 (0.39)
67.2	51.3	456 (0.33)	462 (0.26)	457 (0.33)
62.5	52.0	461 (0.29)	466 (0.24)	461 (0.29)
57.8	52.6	463 (0.28)	472 (0.23)	467 (0.24)
53.1	53.2			472 (0.22)
48.4	53.9	476 (0.18)	481 (0.16)	478 (0.17)
43.2	54.9			484 (0.18)
39.1	55.8	484 (0.11)	493 (0.09)	488 (0.11)
34.4	56.5	490 (0.08)	502 (0.09)	492 (0.09)
29.7	57.2	502 (0.06)	507 (0.05)	498 (0.07)
25.3	57.9	510 (0.05)	516 (0.05)	
20.3	58.7	515 (0.04)	522 (0.03)	504 (0.03)
11.0	60.9	520 (0.02)		

[a] Temperature 25 ± 2 °C. Temperature effects on the position of the fluorescence maximum or the intensity of the emission over this temperature range are small. [b] For details of the 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 Ch. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968), or derived from values in that table by linear interpolation. [e] In nm. [f] ±10% or less, according to reproducibility. Quinine sulfate in 0.1 N H_2SO_4, ϕ_F = 0.55. Data given for experiments carried out without correcting for refractive index or purging by nitrogen. Such purging raises the quantum yields by a small percentage, especially in nonpolar solvents.

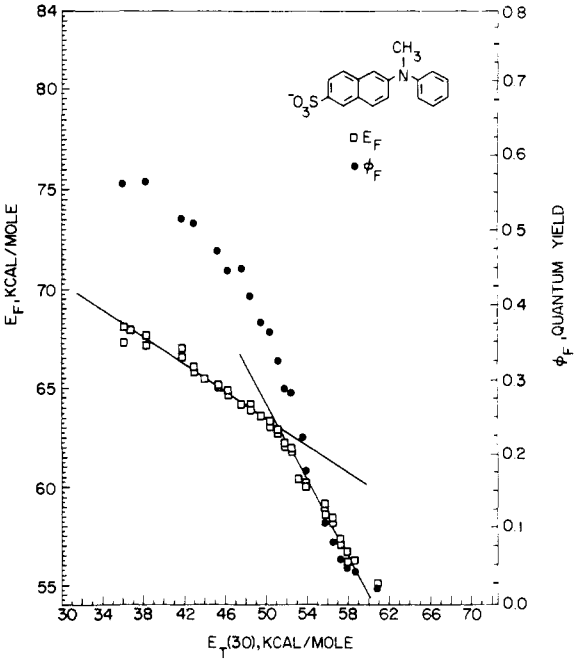
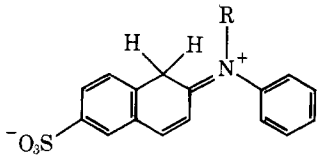


Figure 1. Emission energies (E_F) (in kcal/mol) [from two independent series of solutions] and quantum yields of emission (ϕ_F) for *N*-methyl-2-*N*-phenylamino-6-naphthalenesulfonate (**1M**) (in kcal/mol) plotted against solvent polarity values, $E_T(30)$ for dioxane-water mixtures [cf. C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968)]. Extrapolation of the linear correlation indicated for low-polarity solvents to $E_T(30)$ = 57.0, the value for glycerol as reported in ref 6, yields the predicted emission energy for **1M** in glycerol.

acid revealed that an emission at 400 nm similar to that observed for the **1** series could be observed. The amount of sulfuric acid needed to produce the 400-nm emission increased as the basicity of the ANS derivative decreased, implying that a protonation was involved in the photochemical transformation. The excitation spectrum for the 400-nm emission resembled that for the 405-nm emission of **1M.**

The photochemical product accounted completely for the fluorescence observed for the **1M, 1E,** and **1HE** compounds in glycerol. The emission spectrum had a maximum at 405 nm, the excitation spectrum was identical with that found for the unexpected emission of **1M** and was identical with the absorption spectrum of the photochemical product.

The structures of the photoproducts (**3M, 3E,** and **3HE**) were established by NMR as the protonated betaine [*N*-alkyl (**3M** = *N*-methyl) betaine of 6-sulfonato-3β-tetralenone *N*-phenylimine] shown below. A protonated doubly positive



3

M, R = CH_3; **E**, R = CH_3CH_2; **HE**, R = $HOCH_2CH_2$

naphthalene derivative has been reported by Alder and Goode. In our case, 3-protonation is considered less likely.

The NMR spectrum of a D_2O solution of photoproduct can be divided into two regions, a major one comprising the aromatic and vinylic protons and a minor one composed of R group protons and those of the CH_2 group, including the added

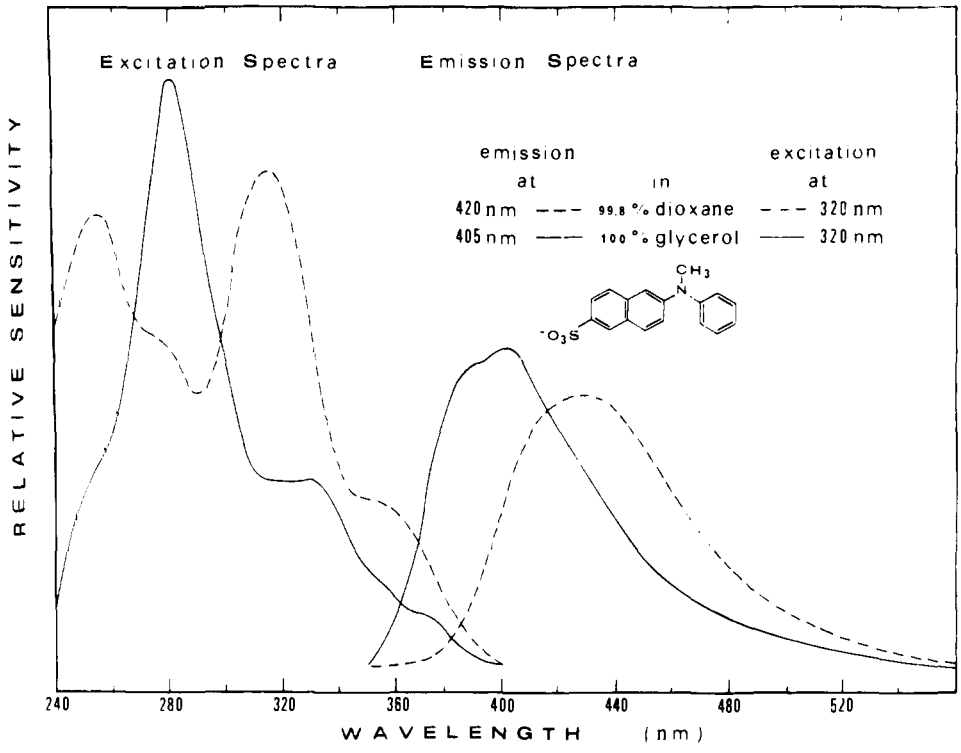


Figure 2. Left: Excitation spectra for the emission of *N*-methyl-2-*N*-phenylamino-6-naphthalenesulfonate (**1M**) in glycerol at 405 nm (—) and in dioxane-water at 428 nm (- - -). Right: Emission spectra for **1M** in glycerol (—) and dioxane-water (- - -) with excitation at 320 nm. Relative heights are chosen arbitrarily and are not to be compared (see text).

proton. The *N*-methyl group was found at δ 2.83 and the CH_2 as two peaks, one hydrogen appearing at δ 2.5, the other at δ 2.1. A monodeuterio compound could be prepared by irradiation of **1M** in 1,2-ethanediol-d_2 as shown by the lack of the hydrogen with δ 2.5 in the NMR spectrum (Figure 3).

The close relationship of the two hydrogens assigned to the CH_2 group of **3HE** was shown by the effect of temperature on the NMR spectrum. The broad bands of the CH_2 hydrogens narrowed at 93 °C to two sets of narrow peaks, and the chemical shifts of the two hydrogens were less different from one another and at slightly lower field (see Figure 3).

The peak assigned to the *N*-methyl group in the NMR spectrum of the photoproduct of **1M** was not present in the NMR spectra for the photoproducts of **1E** and **1HE**, being replaced by peaks in appropriate locations as noted in the Experimental Section.

The photoproducts **3M, 3E,** and **3HE** were solids which did not melt on heating to 250 °C. All had emission maxima at 405 nm in glycerol (a shoulder also appearing at 388 nm) with a fluorescence quantum yield of 0.30. The spatial distribution of photoproduct in glycerol could be monitored after irradiation in the spectrofluorimeter for 5 min at 25 °C using a 20-nm excitation slit. The cell was then removed in a darkened room and the irradiated region observed with an ordinary UV light. The dimensions of the irradiated region (Figure 4) were utilized in obtaining quantitative information on the photoreaction. A similar experiment in which light was introduced from the intense tungsten-iodine (UV visible) source of the Cary Model 17 spectrophotometer at right angles to the direction from which the light from the xenon source of the spectrofluorimeter came revealed that the region used for the absorption of light overlapped with that used for the measurement of fluorescence provided that the viscous solvent was not disturbed in any way. Introduction of another solvent (e.g., water, ethanol) or mixing led to removal of the photoproduct from the light path and the results which puzzled us in our initial work. No doubt the changes noted by Brand and Seliskar come about

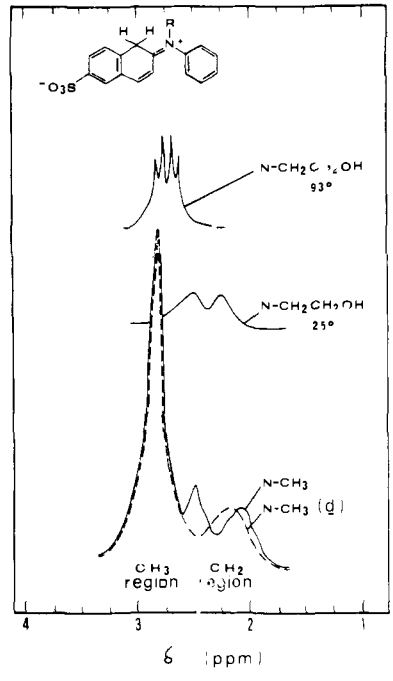


Figure 3. NMR spectra of the *N*-methylbetaine of 6-sulfonato-3β-tetralenone *N*-phenylimine (**3M**) in D_2O at 25 °C for the region between δ 1.5–3.2 (in ppm) along with the deuterated analogue (**3M-***d*) (apparently monodeuterated; for preparation, see text) and the CH_2 region of the *N*-(2-hydroxyethyl) derivative (**3HE**) which shows a marked alteration in spectroscopic pattern on raising the temperature from 25 to 93 °C.

in a similar way as a result of a temperature-induced change in viscosity along with mixing within the cell.

The protonated product **3M** was reconverted slowly to **1M** (TLC and fluorescence characteristics) by boiling with 1 M sodium hydroxide for days. Heating with neutral buffer or with 1 N HCl had no apparent effect.

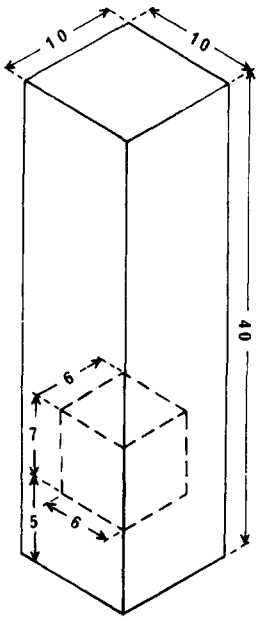


Figure 4. A representation of the irradiated region for a typical *N*-alkyl-2-*N*-phenylamino-6-naphthalenesulfonate (**1**) solution in glycerol placed within the cell compartment of the MPF-4 spectrofluorimeter (slits 20 nm, $\lambda_{excitation}$ 320 nm). The region is located 5 mm above the bottom of the cell. Its dimensions are 6 mm wide, 7 mm high, and 6 mm deep. Visualization was accomplished with a UV lamp used for chromatography after the solution had been irradiated for sufficient time (about 5 min). To check the overlap between the volume probed by the Cary Model 17 beam and that irradiated within the spectrofluorimeter, the cell was turned at right angles to the initial direction and exposed for a long time to the maximum intensity of the excitation wavelength in the cell compartment of the Cary. Exposure to the UV lamp then revealed the coincidence of the irradiated regions. With a little care in moving the cell, this represents a convenient technique for visualizing light paths and irradiated regions.

Quantitative Aspects of Protonated Product (Photoproduct) Formation. Using a wide excitation slit (20 nm), it was possible to convert **1M** in glycerol to the protonated product using irradiation within the spectrofluorimeter over conveniently short times. With care the cell could be transferred to the Cary Model 17 for an absorption spectrum and the transformation followed, as shown by the isosbestic point in Figure 5. The isosbestic point shows clearly that the reaction is a clean conversion of **1** → **3**. Using the measured photon flux, the quantum yield of protonated product formation (ϕ_H) for all three *N*-alkyl derivatives in glycerol was found to be 0.05 ± 0.01. The quantum yield was almost unchanged on lowering the temperature to about 7 °C. Replacing the solvent by its deuterated analogue, glycerol-d_3, had little effect on the quantum yield. The quantum yield was also measured in 1,2-ethanediol (ϕ_H 0.006, see isosbestic point in Figure 5), 1,2-ethanediol-d_2 (ϕ_H 0.005), and 1,2-propanediol (ϕ_H 0.0006), solvents which are less viscous than glycerol. Although the yields are much lower than in glycerol, the results are quite important for the construction of a scheme to cover the behavior of **1M** after the absorption of light.

A brief study of the wavelength dependence (320, 360, 380 nm excitations; slit 20 nm) of the quantum yield of protonated product in glycerol indicated that the dependence was either small or zero.

It must be emphasized that the quantum yield of protonated product in glycerol is so high that even brief exposure to light must be avoided if reliable results are to be obtained in irradiation or fluorescence experiments. Diminishing the viscosity by warming the glycerol, or by the addition of 1,2-ethanediol or ethanol or water, decreases the quantum yield of protonated product formation and makes it easier to observe the expected emission with λ_{max} 470 nm.

Finally, the spectrum expected on the basis of the dioxane–water results (Figure 1)[6] could be obtained. It was necessary to use a solution which had been protected from light and to measure the fluorescence spectrum using a narrow excitation slit minimizing the production of the protonated material during the time in which the spectrum was measured. The λ_{max} for the emission was about 470 ± 2 nm (predicted 468 nm), and the excitation spectrum was identical with the **1** absorption spectrum. The quantum yield of expected emission was about 0.1, considerably lower than that found for compounds in the **2** series in glycerol.[3,6]

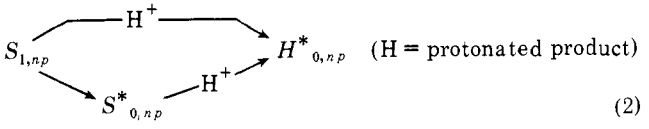
Discussion

With appropriate precautions, the fluorescence of *N*-alkyl-2-*N*-arylamino-6-naphthalenesulfonates in glycerol at 25 °C is that expected on the basis of previous results with ANS derivatives.[3] The sequence of states generated by light absorption in glycerol is summarized in eq 1. The $S_{1,np}$ emission

$$S_{0,np} \xrightarrow{h\nu} S^*_{1,np} \longrightarrow S_{1,np} \xrightarrow{-h\nu} S_{0,np} \qquad (1)$$

in glycerol is almost exactly that predicted from the correlation shown in Figure 1 for emission in the nonpolar region and assigned to the $S_{1,np}$ state. However, the quantum yield for the $S_{1,np}$ emission of **1** in glycerol is low, about 0.1, compared with the 0.4 observed for the $S_{1,np}$ emission of **2** in glycerol. Since the substitution of chlorine or bromine atoms in the 4 position of **1M** leads to little change in fluorescence quantum yield in glycerol[7] (heavy atom effects will be discussed in a separate article), intersystem crossing is not responsible for the low quantum yield. Internal conversion must thus be extremely favorable for $S_{1,np}$ of the **1** series.

ae protonated product (the photoproduct) is produced initially in a ground electronic state, presumably at a high vibrational level. This conclusion follows from the excitation spectrum of the protonated product fluorescence which appears after brief irradiation in glycerol. The excitation spectrum is rather different from the absorption spectrum of the precursor molecule and identical with the absorption spectrum of the protonated product. Thus the emitting state is not produced directly by excitation of the *N*-alkyl-2,6-ANS molecules but via a ground-state molecule which can then undergo the usual absorption and emission processes. This pathway may be expressed as shown in the following equation:



(2)

$$H^*_{0,np} \longrightarrow H_{0,np} \xrightarrow{h\nu} H^*_{1,np} \longrightarrow H_{1,np} \xrightarrow{-h\nu} H_{0,np}$$

The quantum yield of protonated product is substantial, about 0.05, in glycerol. No significant alteration in the yield was achieved by (a) lowering the temperature, (b) substituting glycerol-d_3 for glycerol, or (c) altering the excitation wavelength. On this basis, we may state that the transition state for protonation is very close to the initial state since isotopic substitution does not alter the rate relative to other processes (e.g., vibrational relaxation which should exhibit a small isotope effect), and the activation energy for the proton transfer is similar to that for other processes like vibrational relaxation. We may further infer that vibrationally excited $S_{1,np}$ states do not protonate directly (see eq 2) since this should give rise to a wavelength dependence of the quantum yield for protonation. This last conclusion is reinforced by a consideration of the

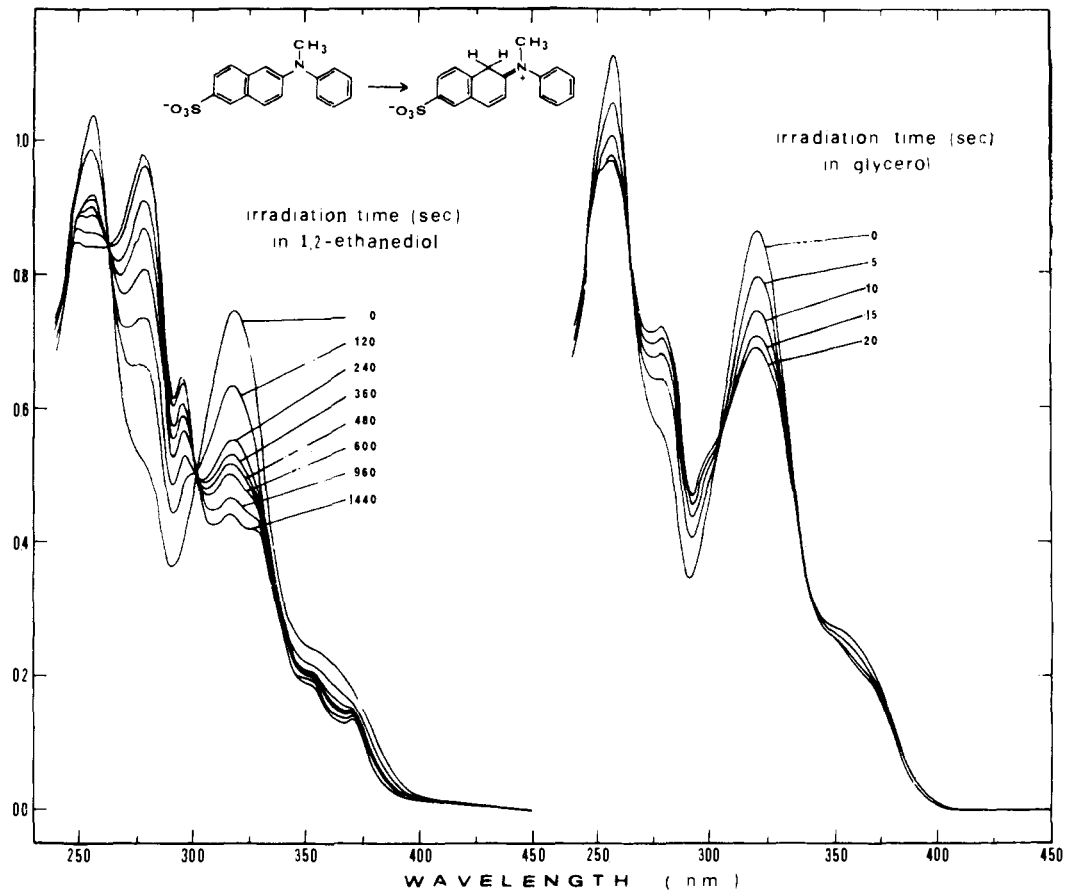


Figure 5. Absorption spectra of *N*-methyl-2-*N*-phenylamino-6-naphthalenesulfonate (**1M**) as a function of irradiation time, followed for the purpose of determining the quantum yield of protonated product (photoproduct, **3M**) formation. Isosbestic points are apparent in both sets of curves. Left: 1,2-ethanediol, 25 °C. Right: glycerol, 25 °C. Excitation wavelength, 320 nm, slit 20 nm.

quantum yields of protonated product in 1,2-propanediol and 1,2-ethanediol.

Moderately viscous solvents were utilized in our previous work[3] to promote charge-transfer light emission at the expense of charge-transfer quenching. The quenching reaction produces the vibrationally excited ground state, $S^*_{0,np}$, by the sequence shown in eq 3. 1,2-Propanediol is more viscous than 1,2-ethanediol and should therefore give rise to a lower yield of $S^*_{0,np}$ than 1,2-ethanediol, relative to charge-transfer light emission. We should thus expect a lower quantum yield of photoproduct in 1,2-propanediol than in 1,2-ethanediol via $S^*_{0,np}$, but a higher yield if protonation occurred via the $S^*_{1,np}$ state. In fact, the yield of protonated product is a factor of 10 *lower* in 1,2-propanediol than in 1,2-ethanediol, and we may now write the pathway shown in eq 4 as the most probable pathway for the formation of the protonated product:

$$S_{1,np} \rightarrow S_{1,ct} \rightarrow S^*_{0,np} \rightarrow S_{0,np} \quad (3)$$

$$S_{1,np} \longrightarrow S^*_{0,np} \xrightarrow{H^+} H^*_{0,np} \longrightarrow H_{0,np} \quad (4)$$

The protonation reaction as well as the considerable stability of the protonated product seems at first sight surprising. Inspection of models, however, reveals a substantial steric hindrance between the *N*-alkyl group and the 1-hydrogen on the naphthalene ring, with the rotation of the *N*-alkyl group clearly restricted. The hindrance is relieved on conversion to the protonated product in which the *N*-methyl group can rotate freely.

The fact that only one hydrogen is missing from the 1-CH_2 group in the monodeuterated product produced by irradiation in 1,2-ethanediol-d_2 implies that the protonation reaction is stereospecific and that the two forms of the product do not interconvert at 25 °C very rapidly. Models indicate that an "axial approach" for the proton is most likely, the incoming hydrogen moving toward a less axial position as the reaction proceeds. It is not possible at this time to specify which hydrogen position is occupied by the deuterium, and further effort is required to elucidate this point.

From single photon counting measurements of lifetimes[8] for closely related compounds and for **1M** in dioxane (99.8%) along with the quantum yield of normal fluorescence in glycerol, we may estimate the nonradiative rate for $S_{1,np}$ in glycerol as 9.5×10^7 s^{-1}. Single laser pulse experiments[9] on **1M** in glycerol showed that the triplet of **1M** was formed in low yield. The rate of formation of $S^*_{0,np}$ from $S_{1,np}$ must be close to the nonradiative rate for the loss of $S_{1,np}$.

The fate of $S^*_{0,np}$ is primarily determined by a competition between vibrational relaxation and protonation. The dielectric relaxation rate[10] for glycerol at 25 °C is ca. 1×10^9 s^{-1}. We assume that the vibrational relaxation rate is ca. two times greater, since the **1M** molecule is different from a solvent molecule.[11] The fraction of $S^*_{0,np}$ which is diverted to protonated product is given by quantum yield of protonated product/quantum yield of nonradiatively formed states or 0.05/0.90 = 0.056. The protonation rate is thus estimated as 1.1×10^8 s^{-1}.

Many other ANS derivatives, especially those substituted in the *N*-aryl ring with strongly electron-supplying groups or bearing alkyl groups in the 2′ position, give rise to protonated products upon irradiation. These will be reported later.

Our previous report that there was a wavelength dependence of the fluorescence maximum[4] must now be regarded as an artifact generated by the variation with wavelength in the

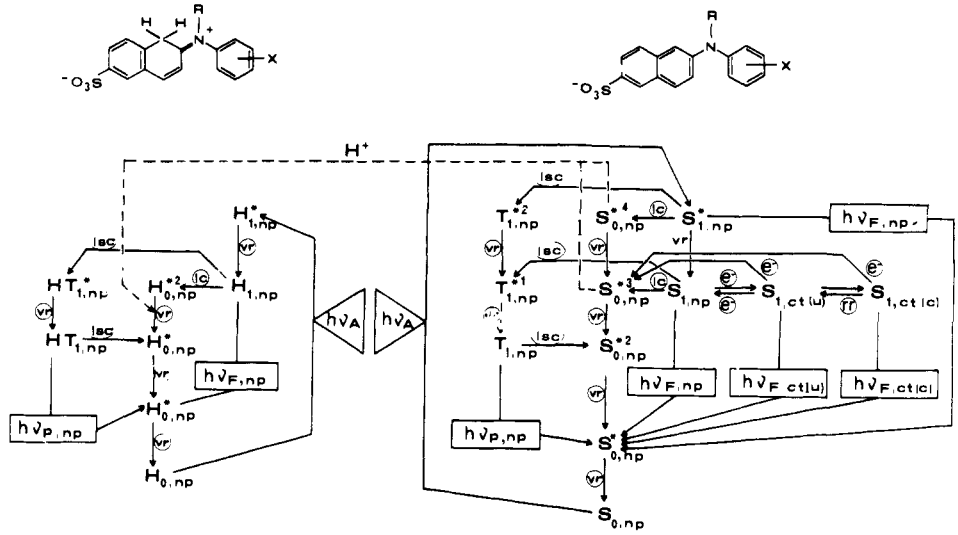


Figure 6. A scheme summarizing the processes which are involved in the excited state behavior of *N*-methyl-2-*N*-arylaminonaphthalene-6-sulfonates (and other 2,6-arylaminonaphthalene-6-sulfonates) (**1M**). Absorption of light by the **1** molecule in the $S_{0,np}$ state [the np character of the ground state has been explained in E. M. Kosower et al., *J. Am. Chem. Soc.*, **97**, 2167 (1975)] (np = nonplanar) and refers to the *N*-aryl group being perpendicular to the plane of the naphthalene ring) leads to a vibrationally excited $S^*_{1,np}$ state. There are at least four decay channels open to the $S^*_{1,np}$ state: (vr) vibrational relaxation, (isc) intersystem crossing, (ic) internal conversion, and ($h\nu$) emission. In glycerol at 25 °C, vr is by far the most important channel, with minor contributions from ic and $h\nu$. (A more quantitative treatment will be presented elsewhere, since it would go beyond the scope of the present paper to do more than cite the figures mentioned in the text). The $S_{1,np}$ state which is formed by vr can, in principle, decay by four channels, but e^-, electron transfer, is minor for reasons discussed in the reference cited above. (The role of e^- in glycerol will be taken up in the more quantitative treatment). The isc process is probably minor in glycerol since heavy atom substituents do not alter the fluorescence quantum yield for compounds lacking the *N*-methyl group. The state lifetime can be estimated from single photon measurements of the lifetime of closely related compounds and is consistent with a small role for the e^- process. (See more quantitative treatment elsewhere.) Emission of light occurs with a quantum yield of ca. 0.1 from **1M**, isc is small, and the major channel for the disappearance of the $S_{1,np}$ state is via ic. The ic produces a state labeled as S^{*3}_0, a vibrationally excited ground state, lower in energy than the vibrationally excited ground state S^{*4}_0 which arises from $S^*_{1,np}$. (The numbering of the vibrationally excited ground states simply indicates the order of the energies, 4 being the highest in vibrational excitation). The S^{*3}_0 state can disappear either through vibrational relaxation or through reaction with a proton donor in the local environment to yield a vibrationally excited form of the ground state of the protonated product (the photoproduct **3M**) labeled here as $H^{*2}_{0,np}$. The S^{*3}_0 state or a state very similar to it in excitation can arise through the quenching reaction of either of the two charge-transfer states, $S_{1,ct(U)}$ and $S_{1,ct(C)}$, an electron-transfer process which returns the charge-transfer states to vibrationally excited ground states. Since formation of the charge-transfer states is minor, the quenching reaction does not increase the amount of S^{*3}_0 states appreciably in glycerol at 25 °C (rr refers to rotational relaxation). After decay of the vibrationally excited H^*_0 states, the $H_{0,np}$ state may absorb light and decay through the sequences indicated on the left side of the scheme. The triplet state, $HT_{1,np}$, has been demonstrated as different from the triplet state of the **1M** type (M. Ottolenghi, unpublished results) using laser pulse photolysis. [H = **3** in this diagram.]

amount of energy absorbed by the experimental solution. The higher the absorption coefficient, the more solute was converted into the protonated product and the closer to 405 nm was the fluorescence maximum. We may conclude that the temperature effect reported by Brand and Seliskar[2a] was also an artifact arising from the same cause.

It is clear that many compounds may give rise to the phenomena which we have described. The factors which affect the course of the excited state processes are many and will be illustrated in the form of an overall scheme which summarizes our present understanding of the excited state behavior of 2,6-ANS derivatives (Figure 6). A more quantitative treatment of some of the kinetic parameters will be presented later.

Experimental Section

Synthesis. *N*-methyl-, *N*-ethyl-, and *N*-(2-hydroxyethyl)-*N*-phenylamino-6-naphthalenesulfonates (as Na^+ salts) (**1M, 1E,** and **1HE**) were prepared by the procedure of Cory et al.[12] and purified carefully by column chromatography (eluent, benzene:methanol 80:20) on silica, followed by crystallization from 1% NaOH. Purity was confirmed by TLC, and structures were established by NMR and UV: NMR (Me_2SO) δ 7.0–8.2 (arom H, naphthalene, aryl, complex pattern), 3.2 (3 H, s, N-CH_3), 1.4 (3 H, t, CH_3 of CH_3CH_2), 4.0 (2 H, q, CH_2 of CH_3CH_2), 4.0 (2 H, t, α-CH_2 of CH_2CH_2OH), 4.1 (2 H, t, β-CH_2 of CH_2CH_2OH); UV λ_{max} (ϵ_{max}) 98% dioxane-water) **1M**: 360 (4200), 318 (18 300), 258 (26 300), **1E**: 365 (4000), 319 (17 100), 258 (15 300), **1HE**: 363 (4900), 320 (20 800), 258 (28 400). All three compounds have a slight shoulder at 280 nm. NMR spectra were measured with a Varian HA-100 NMR spectrometer.

Protonated Product (Photoproduct). (*N*-Methylbetaine of 6-sulfonato-3β-tetralenone *N*-phenylimine, **3M**): **1M** was dissolved in glycerol (dry, for fluorescence microscopy, E. Merck, Darmstadt) or 1,2-ethanediol (ca. 0.1 M material in solution and/or suspension) and the solution irradiated at either 300 or 360 nm in a Rayonet reactor for about 7 days. TLC was used to follow the course of the conversion, showing that starting material had been converted into a slower moving material (eluent, methanol:benzene 40:60 on silica gel). The solvent was removed under high vacuum and the product dried for at least 12 h at 100 °C. **3E** and **3HE** were prepared in the same way in glycerol. NMR (D_2O) δ 6.7–8.3 (arom, vinyl H), **3M**: δ 2.83 (3 H, s, N-CH_3), 2.5 (1 H, broad s), 2.1 (1 H, broad s, CH_2), **3HE**: δ 3.5 (~4 H, broad, CH_2CH_2), 2.5 (1 H, broad s); UV (glycerol) λ_{max} (ϵ_{max}) 371 sh (1200), 330 (6800), 281 (18 900). The NMR spectrum of **3E** was that expected but there was too little material for accurate spectra. At 90 °C in D_2O (spectrum better resolved than at 25 °C): δ 0.89 (~3 H, broad), 2.78 (~2 H, broad), 2.45 (~1 H, broad), 3 (~1 H, broad). The UV spectra of all protonated products were similar, and there appeared to be no solvent effect on the absorption spectrum. NMR spectra were measured with a Bruker WH-90 Fourier transform NMR spectrometer.

Physical Measurements. Absorption spectra were recorded with a Cary Model 17 spectrophotometer. Emission spectra were measured with a Perkin-Elmer Hitachi MPF-4 spectrofluorimeter with a corrected spectra attachment. The light flux on the irradiated area using the spectrofluorimeter was measured with potassium ferrioxalate as an actinometer.[13] Quantum yields of protonated product formation were then followed for solution of **1M, 1E,** and **1HE** in glycerol using 20-nm excitation slit (see Figure 4 for irradiated volume dimensions). Absorption spectra were measured immediately before exposure to specified wavelengths (usually 320 nm) and the course of the photochemical reaction followed by taking further absorption spectra at specified intervals, typically, 5, 10, 15, and 20 s. Transfers of the cell between spectrofluorimeter and spectrophotometer (which are located in the same room) were done very carefully in the dark so as to mini-

mize solution mixing and unwanted irradiation (even exposure to room illumination for some time can lead to appreciable photoreaction). The quantum yields of protonated product were calculated from the equation below, which includes an approximate correction for the change in the amount of light absorbed by the substrate due to product formation (flux = 6.35×10^{-9} eins/cm^2 s at 320 nm). The following symbols were used: D_0, initial optical density of solution; D_t, optical density at time t; D optical density of protonated product after complete conversion; c_{1M}, initial concentration of *N*-alkyl-ANS derivative; v, irradiated volume (see Figure 4); I_0, incident light intensity on area of irradiated volume facing light source; ϵ_{1M}, absorption coefficient for **1M**). All experiments were carried out at 320 nm except for those involving wavelength dependence.

$$\phi_H = \frac{\text{moles of A produced}}{\text{einsteins of light absorbed}} = \frac{\frac{D_0 - D_t}{D_0 - D_\infty} c_{1M} v}{I_0 \left[1 - e^{-\epsilon_{1M} c_{1M} (1 - 1/2 D_0 - D_t / D_0 - D_\infty)} \right]}$$

Experiments in 1,2-ethanediol or 1,2-propanediol were carried out in cells in which the exposed area was smaller than the image of the light on the cell (0.2 cm wide × 2 cm high × 1 cm long). Only 0.4 cm^3 of solution was used, and solutions were mixed before absorption spectra were measured. The protonated products were unchanged on further irradiation in glycerol and disappeared extremely slowly in more fluid solvents like 1,2-ethanediol. However, long irradiation of **1** in methanol caused loss of all long wavelength absorption.

Acknowledgment. The support of the United States-Israel Binational Science Foundation is gratefully acknowledged.

References and Notes

(1) (a) Tel-Aviv University; (b) State University of New York at Stony Brook.
(2) (a) C. J. Seliskar and L. Brand, *J. Am. Chem. Soc.*, **93**, 5414 (1971); (b) H. Dodiuk, unpublished results.
(3) (a) E. M. Kosower, H. Dodiuk, K. Tanizawa, M. Ottolenghi, and N. Orbach, *J. Am. Chem. Soc.*, **97**, 2167 (1975); (b) E. M. Kosower and H. Dodiuk, *J. Phys. Chem.*, in press.
(4) E. M. Kosower and H. Dodiuk, *Chem. Phys. Lett.*, **34**, 253 (1975).
(5) R. W. Alder and N. C. Goode, *J. Chem. Soc., Chem. Commun.*, 109 (1976).
(6) E. M. Kosower and H. Dodiuk, *J. Am. Chem. Soc.*, **96**, 6195 (1974).
(7) E. M. Kosower and H. Dodiuk, *Chem. Phys. Lett.*, **26**, 545 (1974).
(8) H. Dodiuk, unpublished results.
(9) M. Ottolenghi and N. Orbach, Hebrew University, unpublished results.
(10) G. E. McDuffie, Jr., and T. A. Litovitz, *J. Chem. Phys.*, **37**, 1699 (1962).
(11) Based on arguments given by M. D. Magee, *J. Chem. Soc., Faraday Trans. 2*, 929 (1974).
(12) R. P. Cory, R. R. Becker, R. Rosenbluth, and I. Isenberg, *J. Am. Chem. Soc.*, **90**, 1643 (1968).
(13) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

Laser Photolysis Studies of Duroquinone Triplet State Electron Transfer Reactions

R. Scheerer and M. Grätzel*

Contribution from the Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, D 1000 Berlin 39, West Germany. *Received February 20, 1976*

Abstract: A systematic investigation of electron abstraction reactions of triplet duroquinone (DQ^T) has been carried out. A 347.1-nm laser photolysis technique combined with fast conductance measurements and kinetic spectroscopy were used to monitor its reactions with various donor molecules (D). In mixtures of water/ethanol (2:1 v/v) DQ^T abstracts electrons from a variety of substrates such as Fe^{2+}, $Fe(CN)_6^{4-}$, CO_3^{2-}, diphenylamine, and 1,3,5-trimethoxybenzene. Thereby durosemiquinone (DQ^-) and oxidized donor (D^+) is formed. The rate constants for these redox processes are close to the diffusion-controlled limit (10^9-10^{10} M^{-1} s^{-1}) except for D = CO_3^{2-}, where $k = 7 \times 10^7$ M^{-1} s^{-1}. With all donors conversion of DQ^T into DQ^- was quantitative. DQ^T in the H_2O/EtOH mixture also abstracts electrons from ethanol itself. This quenching reaction occurs at a relatively slow rate and yields only ca. 20% DQ^-. Similarly DQ^T in acetone solution abstracts electrons from the solvent, the pseudo-first-order rate constant being 5×10^4 s^{-1}. However, in *n*-hexane DQ^T disappears predominantly via a bimolecular triplet-triplet annihilation process. Anionic micelles were found to accelerate markedly the electron transfer from Fe^{2+} to DQ^T. These results are discussed in terms of the excited state nature of DQ^T and current theories of electron transfer reactions.

Quinoid compounds undergo a manifold of photochemical reactions which have been dealt with recently in a comprehensive review.[1] Among them processes related to the photodeterioration of fabrics and photobiological functions of quinones have received particular attention. In this field photochemical pathways leading to reduction of the quinone play a prominent role. In order to establish the basic mechanism of the latter photoreduction process, several investigations with model compounds, in particular duroquinone,[2-7] have been carried out. Durosemiquinone radicals have been identified as intermediates and triplet state duroquinone as their precursor. The conversion of duroquinone triplets into semiquinone radicals is presently believed to occur via hydrogen abstraction from the solvent molecules.

Our current interest in photo redox processes as possible means of light energy utilization has prompted us to inquire into electron abstraction reactions of quinoid compounds. These studies aim at exploring sensitizers suited for photodecomposing water into oxygen. The present paper reports on laser photolysis studies of redox reactions in solutions in which triplet duroquinone acts as an electron acceptor. The strongly oxidizing nature of the triplet state manifests itself through ready occurrence of electron abstractions from diverse substrates such as Fe(II), trimethoxybenzene, ethanol, and acetone. These results will be subject to an analysis based on current theories of electron transfer reactions in liquids.

* Address correspondence to this author at Ecole Polytechnique, Departement de Chimie-Physique, CH-1007 Lausanne, Switzerland.

Experimental Section

Materials. Duroquinone (Aldrich, Europe, >99.9%) was further purified by recrystallization from hexane. Its concentration in solution was maintained at 10^{-3} M throughout the experiments. Sodium lauryl sulfate (Merck, "for tenside investigations") was purified by multiple recrystallization from ethanol/ether mixtures. Acetone (Merck p.a.) was fractionally distilled from dehydrated Na_2SO_4; *n*-hexane (Philips, research grade) was purified by column chromatography. Diphe-