Photoexcited Proton Transfer from Enhanced Photoacids

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Abstract: Naphthols with electron-withdrawing groups such as cyano or methanesulfonyl at C-5 and C-8 exhibit greatly enhanced photoacidity. This increase in photoacidity enables the substituted naphthols to undergo excited-state proton transfer (ESPT) in alcohols and Me_2SO in the *absence* of water. In aqueous tetrahydrofuran solution, efficient proton transfer to water occurs at much lower water concentrations than with the parent naphthol, and the kinetics of proton transfer indicate that a smaller water cluster is involved.

Introduction

Hydroxyarenes undergo an enhancement of acidity upon photoexcitation.[1] Associated with the enhanced acidity as measured by pK_a^* and predicted by the Förster equation, eq 1,

$$pK_a^* = pK_a + (E_{A^-} - E_{HA})/2.3RT \qquad (1)$$

is a shift in anion emission to longer wavelengths, relative to the conjugate acid. Therefore, hydroxyarenes are ideal substrates for examining fundamental aspects of proton transfer using time-resolved fluorescence measurements. Unfortunately, a limitation of these studies is the relatively modest change in acidity, ca. 6−8 pK_a units, which occurs upon photoexcitation with conventional hydroxyarenes. This limitation confines most photophysical investigations to solvents in which proton transfer competes with the ca. 10 ns decay lifetime, i.e., to aqueous solvents.

In order to expand the range of photoacids available for fundamental studies in proton-transfer kinetics, we have embarked on a program to define the factors responsible for photoacidity and to design and synthesize new photoacids with enhanced proton donor ability. Using the well-studied 1- and 2-naphthols as our starting points, we have observed that substitution by electron-withdrawing groups on the distal ring provides the most significant enhancement.[2] We report here the syntheses of 5,8-dicyano-1-naphthol (DCN1) and 5,8-dicyano-2-naphthol (DCN2) and provide details of the syntheses of the previously reported monocyanonaphthols.[2] We further provide a rationale for their design, and describe their photophysical behavior. The behavior of DCN2, in particular, suggests that excited-state pK_a may also affect the size of water clusters involved in proton transfer in aqueous solvents.

Background

The reason for the enhanced acidity of hydroxyarenes upon photoexcitation can most clearly be seen by an appeal to Hückel molecular orbital theory applied to the conjugate base. In its simplest form, the conjugate base of a hydroxyarene may be viewed as a derivative of an odd-alternant hydrocarbon anion,

which has a nonbonding molecular orbital (NBMO) with a large coefficient on oxygen. In the one-electron representation, photoexcitation removes an electron from the NBMO and places it in the lowest unoccupied molecular orbital (LUMO), which, in general, will not be localized on oxygen. This charge redistribution has two immediate effects. First, the basicity at oxygen is reduced, or equivalently, the acidity of the conjugate acid is enhanced, forming an "intramolecular charge-transfer" state.[3] Second, the basicity at carbons that have high LUMO coefficients will be increased. The degree to which these two effects will have photophysical consequences depends upon the nature of the LUMO.

Naphthalene has two spectroscopic states, L_a and L_b, which are degenerate at the Hückel level. Addition of oxygen to the naphthalene system polarizes the ground state electron density toward oxygen and the excited-state electron density toward the distal ring, diminishing the electron density on oxygen and, hence, oxygen basicity. The nature of the charge polarization depends upon the site of oxygen substitution. The comparison between 1-naphthol and 2-naphthol is particularly instructive. First, 1-naphthol has an excited state which is more acidic in water by ca. 2 pK_a units than that of 2-naphthol. Second, the conjugate base of 1-naphthol undergoes rapid proton quenching, apparently by protonation at positions 5 and 8.[4] The enhanced acidity of 1-naphthol relative to 2-naphthol, as well as its quenching behavior, has been associated with the relative energies of the L_a and L_b states. The L_a state is lower in energy in the case of 1-naphthol, and the L_b state is lower in the case of 2-naphthol. The L_b state is a more diffuse state, which is exhibited in both diminished acidity and reduced proton quenching for 2−naphthol.

Proton transfer to water, despite its fundamental significance, is an enormously complicated problem. Water itself has a relatively low gas-phase proton affinity (166.5 kcal/mol) compared to other proton acceptors such as methanol (181.9 kcal/mol), acetonitrile (188.4 kcal/mol), and tetrahydrofuran (198.8 kcal/mol).[5] However, the relatively low proton affinity of water is compensated in solution by the formation of extensive hydrogen-bonded networks,[6] and makes simple correlations with gas-phase acidities problematic. Given the modest pK_a enhancement observed upon photoexcitation for unsubstituted naphthols, Robinson,[7] Shizuka,[8] Kelley,[9] and the Huppert group[10] have observed significant nonlinear dependence of the

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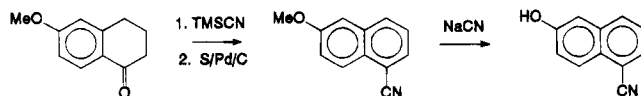
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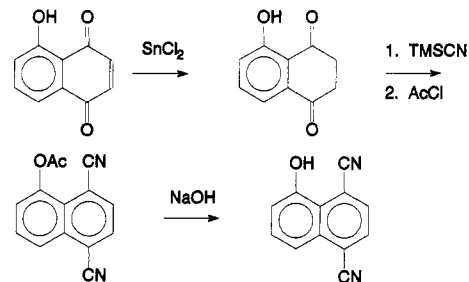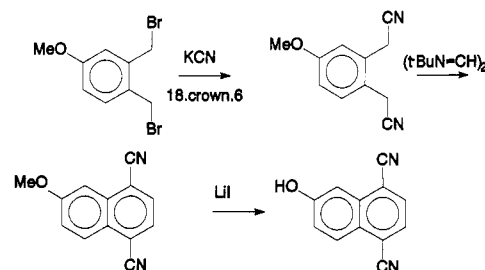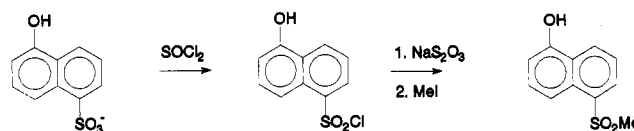

Figure 1. Synthesis of 5-cyano-2-naphthol (5CN2).

rate of proton transfer upon water concentration, a phenomenon which has seen various explanations. For weak proton donors in particular, Robinson and co-workers have attributed the nonlinear concentration dependence to the requirement for the formation of water clusters in the proton-transfer step and have interpreted this data as requiring the intervention of a minimum cluster size of four water molecules, a phenomenon which Robinson has emphasized[7,11] is relevant to the weak acid regime represented by 2-naphthol. Only water molecules can undergo the translational/rotational motion required for cluster formation within the lifetime of the excited state. Although this interpretation has been challenged by Huppert and Agmon,[12] at least in the low-water high-methanol concentration regime, the difference in proton transfer efficiency is related to the diminished cluster stability when methanol replaces the last water molecule. Recently, our studies on proton-transfer kinetics when an *intramolecular* solvent cluster is involved show diminished entropic requirements for proton transfer.[13]

The enhancement of acidity by the L_a state in 1-naphthol suggested that substitution at C-5 and/or C-8 by an electron-withdrawing group should provide the greatest excited-state acidity enhancement, at least for 1-naphthol. However, in order to probe this question in greater detail, we required naphthols substituted at C-6 and C-7 as well. The choice of electron-withdrawing groups was dictated by both availability and photostability. Unfortunately, the strongest electron-withdrawing groups, e. g., nitro, are photolabile in the presence of strong electron donors, e.g., naphtholate. Thus, we elected to synthesize naphthols substituted by cyano and, in one case, methanylsulfonyl.

Results

Synthesis. Syntheses of 5-cyano-2-naphthol (5CN2), 6-cyano-2-naphthol (6CN2), 7-cyano-2-naphthol (7CN2), 8-cyano-2-naphthol (8CN2), and 5-cyano-1-naphthol (5CN1) were readily achieved by sodium cyanide/Me₂SO demethylation of the corresponding methyl ethers. The methyl ethers in turn were generated in high yield by cyanosilylation of a methoxytetralone and aromatization of the resulting dihydrocyanomethoxynaphthalenes with sulfur/Pd−C (see Figure 1). 5,8-Dicyano-1-naphthol (DCN1) was prepared by a similar reaction of

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Figure 2. Synthesis of 5,8-dicyano-1-naphthol (DCN1).

Figure 3. Synthesis of 5,8-dicyano-2-naphthol (DCN2).

Figure 4. Synthesis of 5-(methanesulfonyl)-1-naphthol (MSN1).

Table 1. Properties of Cyano-2-naphthols

	2-naphthol	5CN2	8CN2	DCN2
λ_{max} (neutral, abs, Me₂SO)	334	337	342	351
λ_{max} (neutral, em)	360	419	424	512
λ_{max} (anion, abs)	384	371	382	394
λ_{max} (anion, em Me₂SO)	449	552	515	616
pK_a (H₂O)	9.45	8.75	8.35	7.8
pK_a^* (Förster)	2.8	−1.2	−0.4	−4.5
pK_a^* (fluorescence)	2.8	1.5	0.6	a
τ, ns (neutral, THF)	8.6	3.2		12.3
τ, ns (anion, Me₂SO)[b]				4.3

[a] Could not be determined (see text). [b] Determined for DCN2 only.

trimethylsilyl cyanide with 5-hydroxy-1,2,3,4-tetrahydronaphthalene-1,4-dione (dihydrojuglone) and isolated as its acetate (see Figure 2). An alternative synthesis was employed for 5,8-dicyano-2-naphthol (DCN2). This synthesis involved condensation of 4-methoxybenzene-1,2-bisacetonitrile[14] with glyoxal in its bis(*tert*-butylimine) protected form, followed by demethylation in similar fashion (see Figure 3).

5-(Methanesulfonyl)-1-naphthol (5MSN1)[15] was prepared by treatment of 5−hydroxy-naphthalene-1-sulfonate with thionyl chloride followed by reduction of the sulfonyl chloride with sodium sulfite and alkylation of the resulting sulfinate anion (see Figure 4).

Absorption and Emission Spectroscopy. The effect of cyano substitution was, in each case, a small (3−17 nm) bathochromic shift in the absorption maximum and a larger shift in the emission maximum relative to the parent naphthol (see Table 1). In alcoholic solution, an additional emission band for the substituted naphthols was observed which was absent in the parent naphthols. This additional emission band varied

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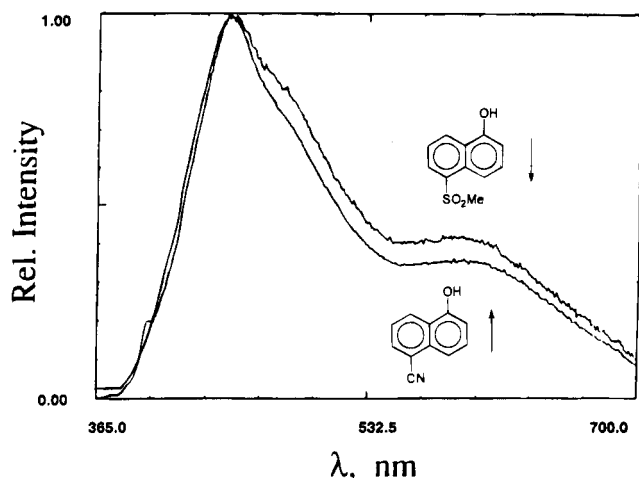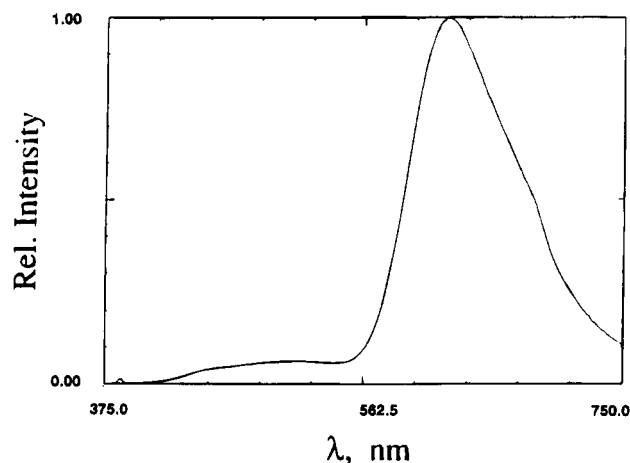**Figure 5.** Emission from 5DN1 and 5MSN1.

Figure 6. Emission of DCN2 in Me₂SO.

Figure 7. Stern—Volmer quenching of 5,8-dicyano-2-naphthol.

Figure 8. Quenching of naphthol fluorescence by water in aqueous tetrahydrofuran.

in position and relative intensity with the site of cyano and hydroxy substitution. Both emission bands had identical excitation spectra which corresponded in shape and excitation maxima to the absorption spectra. That this additional band represented a Förster shift, i.e., emission from the conjugate base after adiabatic deprotonation, was confirmed by comparison of the emission bands with those obtained by excitation of the sodium salts of the naphthols. In the case of the sodium salts, the excitation and absorption bands were identical. Little difference was observed between the positions or intensities of emission from 5CN1 or 5MSN1 (see Figure 5).

Both 1- and 2-naphthols exhibit mainly anionic emission in water. However, emission from 1-naphthol in water is considerably attenuated. Similar quenching behavior was exhibited by 5-cyano-1-naphthol and 5,8-dicyano-1-naphthol, which had only weak emission in neutral aqueous or alcoholic solution. In contrast, all cyano-subsituted 2-naphthols, as well as MSN1, exhibited strong emission in aqueous solution, characterized by anionic emission at neutral pH. Other solvents were effective in producing anionic emission from the cyanonaphthols, most notably among these dimethyl sulfoxide. DCN2 produced nearly exclusively anionic emission in Me₂SO (see Figure 6). In contrast, DCN2 produced only neutral emission in tetrahydrofuran. Thus, tetrahydrofuran provided a useful miscible solvent for investigating the emission characteristics of mixed solvent systems and examining the molecularity of proton transfer. Addition of water or dimethyl sulfoxide to tetrahydrofuran solutions of all cyanonaphthols produced an increase in anionic emission at the expense of neutral emission. Such results are most easily visualized using Stern—Volmer kinetics,
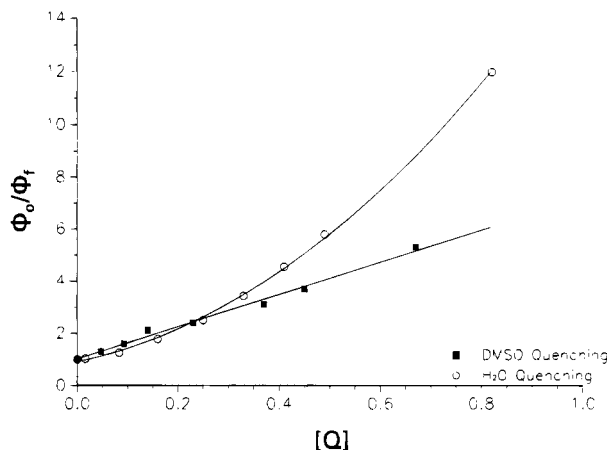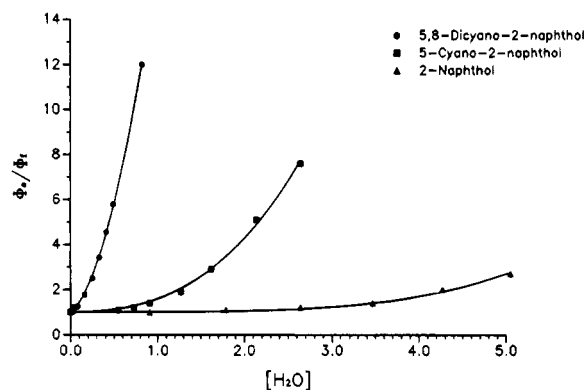
viewing the proton acceptor as a quencher of neutral emission. A plot of Φ_o/Φ_f vs quencher concentration for DCN2 yielded a linear plot in the case of dimethylsulfoxide but an upwardly curved plot in the case of water with tetrahydrofuran as solvent (see Figure 7).

The quenching of the substituted naphthol fluorescence, in addition to providing upwardly curved Stern—Volmer plots, was highly dependent upon the degree of substitution, with the greatest quenching for 5,8-dicyano-2-naphthol (DCN2) and the least for 2-naphthol itself (see Figure 8).

pK_a Measurements. Ground-state pK_a measurements were carried out by spectrophotometric titration of the neutral aborption. The titration curve was fit using nonlinear regression analysis to the usual theoretical expression (eq 2, where K is

$$I = KI_o/([H^+] + K) \qquad (2)$$

the acid dissociation constant and I_o is the emission intensity in the high pH regime). The ground-state pK_a values showed only a small effect for cyano substitution, commensurate with substitution distal to the hydroxyl group. The apparent pK_a^* values were determined by fluorescence titration of anion emission. Again, the pK_a^* values were determined from the nonlinear regression analysis. Figure 9 compares the absorption and emission titration curves and best fit to the data for 5- and 6—cyano-2-naphthol. The pK_a^* values were also computed using the Förster cycle from both fluorescence and absorption data (see Table 1). In the case of DCN2, it was not possible to determine pK_a^* by fluorescence titration, since at low pH precipitation of the insoluble neutral reduced the emission to undetectable levels.
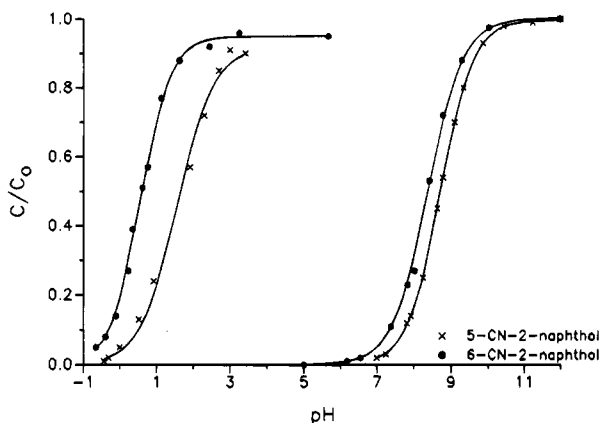
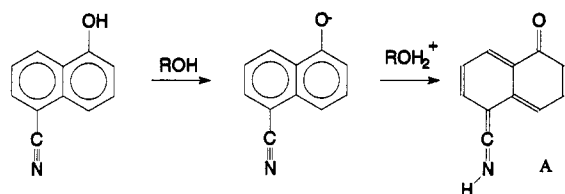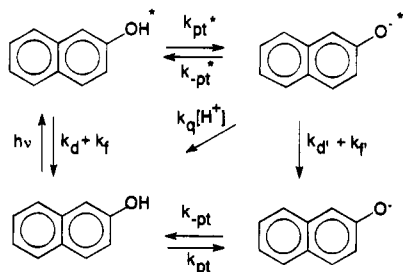**Figure 9.** Absorption and emission titration of 5- and 6-cyano-2-naphthols.

Figure 10. Quenching of 5-cyano-1-naphthol (5CN1).

Scheme 1. Decay Mechanisms in 2-Naphthols

Discussion

Proton transfer represents but one of several competing decay pathways for photoexcited naphthols, including proton-induced quenching (see Scheme 1). The "true" excited-state pK_a, pK_a^*, represents the negative log of the equilibrium constant for adiabatic forward and reverse proton transfer, i.e., k_{pt}^*/k_{-pt}^*. Excited-state pK_a measurements are complicated by competing decay processes, including fluorescence (k_f) and nonradiative decay (k_d) (see Scheme 1). In the case of naphthols, an additional quenching process (k_q) which is dependent upon proton concentration, has also been observed. This additional quenching process has been particularly problematic for 1-naphthol, which apparently undergoes proton transfer through a mechanism involving protonation at C-5 or C-8.[4] For example, protonation at C-8 can proceed adiabatically to form the excited state of 5H-naphthalene-1-one followed by rapid internal conversion or may proceed diabatically. Such quenching is apparently in evidence for 5-cyano-1-naphthol and 5,8-dicyano-1-naphthol. Although speculative, we propose the intervention of structures of type **A** (see Figure 10). In any event, proton-induced quenching complicates the analysis of the photoacidities of 1-naphthols, given the data at hand. Therefore, we devote the rest of the discussion to the substituted 2-naphthols.

Given the processes competing with proton transfer, the pK_a^* values determined by fluorescence titration must be considered as lower limits. The pK_a^* values determined by the Förster equation using either absorption or emission maxima are also approximate, since they include ground-state acidities involving

molecular geometries and solvation changes considerably different from those in the excited state. For instance, 7-cyano-2-naphthol ($pK_a = -1.3$) appears more acidic than 8-cyano-2-naphthol by Förster titration, yet the latter appears more effective at protonating dimethyl sulfoxide.[2] Indeed, the 5,8-dicyano-2-naphthol, by either fluorescence titration or solvent quenching, appears to be the most acidic naphthol to date.

With the availability of naphthols with enhanced acidities, the kinetics of proton transfer to less basic solvents than water may be studied and the nature of proton transfer to water itself in the strong acid regime may be clarified. The Stern—Volmer treatment of proton transfer to dimethyl sulfoxide in tetrahydrofuran solvent reveals bimolecular pseudo first-order kinetics involving a single molecule of dimethyl sulfoxide as acceptor. This first-order behavior presumably mirrors the absence of hydrogen-bonding networks in the non-protic medium. In contrast, proton transfer to water is considerably more complicated.

Robinson[11,16] and others have proposed that the kinetics of proton transfer from weak acids to water in aqueous hydroxylic solvents require that a water cluster be the acceptor. They further note that the size of the cluster is of order 4 ± 1, which presumably reflects the thermodynamic driving force for solvation of the proton during proton transfer from a weakly acidic proton donor such as 2-naphthol. Although such clustering is possible in principle for the alcohols, the larger entropic requirements and enhanced rotational barriers for alcohol clusters do not allow proton transfer to compete. The fact that the cyanonaphthols transfer protons in the absence of water reflects the less stringent requirement for a proton cluster for strong acids and confirms that methanol can serve to solvate a proton in such reactions, as Agmon and Robinson have noted.[11,12] Our studies did not use the hydroxylic methanol, but tetrahydrofuran, which has an even higher proton affinity than methanol. In the case of methanol as solvent, one can argue that solvation of the proton by methanol occurs at the expense of extended hydrogen bonds to bulk solvent. In the case of tetrahydrofuran, for which a hydrogen-bonded network is unavailable, cluster formation becomes more plausible. Studies on the kinetics of proton transfer to anhydrous alcohols are in progress.

The kinetics of proton transfer from photoexcited 2-naphthol in aqueous solvents are complicated. For this weak photoacid, Robinson has developed a theory, based upon the Markov random walk model, which allows the modeling of the Stern—Volmer data. In the case of 2-naphthol in tetrahydrofuran, although the kinetics are apparently still complex,[17] we were able to fit the Stern—Volmer data to the simple fourth-order expression we would expect from the tetramer model, eq 3, where k_{dt} is the decay rate ($= k_d + k_f$) in the absence of water and k_w is the water-dependent component of the decay rate. However, quenching of the emission of 5-cyano-2-naphthol and 5,8-dicyano-2-naphthol was modeled by a second-order expression, eq 4 (see Figure 8). Thus, we agree with Robinson's

$$k_{dt} = k_d + k_w[H_2O]^4 \tag{3}$$

$$k_{dt} = k_d + k_w[H_2O]^2 \tag{4}$$

assessment[11] that the presumed involvement of a water tetramer in proton transfer in competition with excited-state deactivation is at best valid only for relatively weak acids with $pK_a^* > 1$.

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(17) Robinson, G. W. Private communication.

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This conclusion is also in concert with the proposal of Suwaiyan et al.,[18] who have suggested that solvent clustering may operate for proton transfer from poor excited-state proton donors, e.g., 2-naphthol, while solvent reorientation is dominant for strong excited-state proton donors, e.g., our cyanonaphthols. Again, our previous studies using intramolecularly solvated naphthols suggest that solvent reorganization plays the dominant role.[13]

The apparent size of the water cluster is a function of the acid strength of the proton donor and the lifetime of the excited state of the proton donor. This size is a kinetic consequence of the thermodynamics of proton solvation. Although the solvation energy of a proton in bulk solvent is only crudely approximated by gas-phase data, some insight can be gained by examining the gas-phase solvation enthalpies of solvent clusters. According to Meot-Ner, the gas-phase solvation enthalpy of a proton by water is 166.5 kcal/mol for the first water molecule, 31.8 kcal/mol for the second, 19.0 kcal/mol for the third, and 17.6 kcal/mol for the fourth.[19] Of course, the first number is the proton affinity of water and represents the formation of the stable H_3O^+ molecule. In order to compete with excited-state decay (10^8 s^{-1}), proton transfer must occur near the diffusion-controlled limit with considerable reorganization of the solvation shell. However, complete hydration of the proton may not be required as the thermodynamics of proton transfer, as measured by pK_a, become more favorable. In other words, this is simply another example in support of the Hammond postulate. For weak acids, the transition structure resembles the product, a solvated proton. For strong acids, the transition structure resembles the reactants, a solvated naphthol. Although in principle a strong acid might transfer a proton directly to a single water molecule, in practice the limiting form of water in non-hydroxylic organic solvents is as a dimer.[20] We would not, therefore, anticipate proton transfer kinetics of order lower than two with respect to water.

Finally, we observe, on the basis of our limited data, that the enhanced acidities of the substituted naphthols appear to follow a Hammett relationship. Thus, both CN and MeSO$_2$, with Hammett substituent constants σ of 0.70 and 0.73, respectively, have nearly identical effects on the photoacidity of 1-naphthol. Moreover, the photoacidity of DCN2, $pK_a^* = -4.5$, is within experimental error of that determined by a straightforward application of a linear free energy relationship to the photoacidities of 2-naphthol, 5CN2, and 8CN2, namely, 2.8 − 4.0 − 3.2 = −4.4. Thus, the simple model of first excited singlet states of 1- and 2-naphthols as intramolecular charge-transfer states[3] appears vindicated.

Conclusions

The molecularity of water in proton-transfer reactions is a function of the acidity of the proton donor. For weak photoacids such as 2-naphthol, formation of water clusters or, more plausibly, extensive hydrogen-bonded networks during proton transfer presents a probable explanation for the high-order dependence on water concentration. For strong photoacids such as the cyanonaphthols, for which solvent reorganization is less critical, water dimers can be effective proton acceptors.

Experimental Section

Materials. 4-Methoxybenzene-1,2-diacetonitrile was synthesized by a modification of a patent procedure[12] which eliminated one of the intermediate steps. Tetrahydrofuran was distilled from benzophenone

ketyl. Me$_2$SO was distilled from calcium hydride. The monocyanonaphthols were all synthesized by variations of the procedure reported here for 8-cyano-2-naphthol (8CN2).

1-Cyano-7-methoxynaphthalene. Trimethylsilyl cyanide (4.25 mL, 31.9 mmol) was added to 7-methoxy-1-tetralone (5.00 g, 28.4 mmol) under argon over a period of 5 min. Boron trifluoride etherate (150 μL) was added, and the solution was heated at 60 °C for 2 h. An additional 100 μL of boron trifluoride etherate was added and the solution heated at 90 °C for 2 h. After cooling, pyridine (40 mL) and POCl$_3$ (4.5 mL) were added, a distillation head was attached, and about 30 mL of solution was removed by slow distillation (2−3 h). The cooled solution was poured into 200 mL of ice and the mixture extracted 3 times with 25% EtOAc/hexane. The combined organic solutions were washed with water, aqueous 1 M HCl, and water and dried (Na$_2$SO$_4$). After filtration, the filtrate was reduced to ca. 25 mL and filtered through about 10 g of alumina. The alumina was washed with additional 25% ether/hexane, and the combined filtrate was evaporated to leave 3.45 g of gummy colorless crystals with a ^{1}H NMR spectrum corresponding to 1-cyano-3,4-dihydro-7-methoxynaphthalene. An additional 0.557 g of yellow material was recovered by washing with ether and appeared, by ^{1}H NMR spectroscopy, to contain both dihydrocyanonaphthalene and the aromatized naphthalene derivative.

Aromatization of the dihydronaphthalene was accomplished by stirring 3.19 g (17.2 mmol) of the above product, powdered sulfur (0.59 g, 18 mmol), and 5% Pd−C catalyst (0.35 g) under argon at 190−200 °C for 2 h. The cooled mixture was dissolved in ether, and the mixture was filtered through 5 g of alumina which was washed subsequently with ether until no more solid eluted. The combined ether solutions were washed with water, aqueous 10% KOH solution, and water and dried (Na$_2$SO$_4$). Vacuum evaporation of solvents afforded 2.96 g (16.2 mmol, 57%) of an orange solid containing ca. 7% of the dihydronaphthalene. A purified sample had mp 77−79 °C; ^{1}H NMR (CDCl$_3$) δ 3.99 (s, 3), 7.26 (dd, 1, J = 2.4, 7.3 Hz), 7.38 (dd, 1, J = 7.2, 8.2 Hz), 7.47 (d, 1, J = 1.3, 7.2 Hz), 7.82 (d, 1, J = 9.04 Hz), 7.88 (dd, 1, J = 1.3, 7.3 Hz), 8.00 (d, 1, J = 8.2 Hz); IR (KBr pellet) 2210, 1630, 1470, 1435, 1265, 1260, 1205, 1025, 825 cm^{-1}.

8-Cyano-2-naphthol (8CN2). Sodium cyanide (2.13 g, 43.4 mmol) and 1−cyano-7-methoxynaphthalene (1.56 g, 8.55 mmol) were stirred in Me$_2$SO (16 mL) under argon at 160−170 °C for 12 h. The dark green mixture was poured into ice−water, and 20 mL of 6 N HCl was added (**Caution!** HCN gas evolves). The mixture was extracted twice with EtOAc. Combined EtOAc solutions were extracted three times with aqueous 10% KOH solution. The combined KOH solutions were acidified with cold 6 N HCl solution and extracted twice with EtOAc. The combined EtOAc solutions were washed twice with aqueous saturated NaCl solution and dried (Na$_2$SO$_4$). Vacuum evaporation of solvents left 1.25 g of brown solid. This material was sublimed at 160 °C, 0.2 Torr, to yield 1.05 g (6.2 mmol, 73%) of 8-cyano-2-naphthol (8CN2) as a yellow solid. In other preparations, isolation without extraction with aqueous KOH gave nearly quantitative material recovery of a slightly less pure product. For spectroscopic investigations, samples were purified by high-performance liquid chromatography to yield colorless crystals of 8CN2: mp 194−195 °C; ^{1}H NMR (acetone-d_6) δ 2.92 (s, 0.7, OH), 7.33 (dd, 1, J = 2.4, 9.0 Hz), 7.45 (dd, 1, J = 7.3, 8.2 Hz), 7.51 (d, 1, J = 2.1 Hz), 7.97 (m, 2), 8.16 (d, 1, J = 8.3 Hz), 9.36 (s, 0.2, OH); IR (KBr pellet) 3280, 2240, 1630, 1600, 1465, 1385, 1240, 1200, 858, 830 cm^{-1}; UV (98% water, 2% ethanol) λ_{max} 218 nm (ϵ 36 800), 231 (40 200), 288.5 (4370); UV (EtOH) λ_{max} 288 nm (ϵ 4070), 300 (4100), 349 (5420); MS m/z (rel abund) M$^+$ 169 (100), 140 (29), 114 (17). Anal. Calcd for C$_{11}$H$_7$NO: C, 78.17; H, 4.17; Found: C, 78.12; H, 4.19.

5-Cyano-2-naphthol (5CN2). 5-Cyano-2-naphthol was prepared in a manner similar to that used to prepare 8CN2. Orange prisms were obtained in 93% yield. The solid was purified by sublimation (0.3 Torr, 130−140 °C) to give a 71% yield of purified 5-cyano-2-naphthol: mp 179−180 °C; ^{1}H NMR (acetone-d_6) δ 2.85 (s, 0.5, OH), 7.40 (m, 2), 7.57 (dd, 1, J = 7.1, 8.4 Hz), 7.84 (dd, 1, J = 1.1, 7.1 Hz), 8.08 (d, 2, J = 9.1 Hz), 9.15 (s, 0.4, OH); IR (KBr pellet) 3100−3400 (br), 2220, 1610, 1465, 1385, 1230, 1205, 845, 785, 740 cm^{-1}; UV (ethanol) λ_{max} 237 nm (ϵ 20 300), 293 (2180), 304 (2400), 343 (1630); MS m/z (rel abund) M$^+$ 169 (100), 140 (38), 114 (16). Anal. Calcd for C$_{11}$H$_7$NO: C, 78.17; H, 4.17. Found: C, 78.04; H, 4.16.

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6-Cyano-2-naphthol (6CN2). 2-Cyano-6-methoxynaphthalene (Aldrich) was converted to 6CN2 in a manner analogous to that used for 8CN2. Yellow crystals were obtained in 62% yield. A sample was purified by sublimation, followed by crystallization from EtOAc/hexane to leave colorless prisms: mp 163−164 °C; ^{1}H NMR (acetone-d_6) δ 2.83 (s, 3, OH and H_2O), 7.31, (m, 2), 7.61 (dd, 1, J = 1.7, 8.6 Hz), 7.87 (d, 1, J = 8.6 Hz), 7.96 (d, 1, J = 9.8 Hz), 8.33 (s, 1), 9.28 (s, 0.4, OH); IR (KBr pellet) 3200−3500 (br), 2220, 1630, 1480, 1285, 1160, 860 cm^{-1}; UV (ethanol) λ_{max} 243 nm (ϵ 20 000), 305 (8890), 339 (2080); MS m/z (rel abund) M$^+$ 169 (100), 140 (38), 114 (11). Anal. Calcd for $C_{11}H_7NO$: C, 78.17; H, 4.17. Found: C, 78.15; H, 4.23.

7-Cyano-2-naphthol (7CN2). 2-Cyano-7-methoxynaphthalene, mp 75−77 °C, was prepared from 7-methoxy-2-tetralone in a manner similar to that used to make 1-cyano-7-methoxynaphthalene: ^{1}H NMR (CDCl$_3$) δ 3.95 (s, 3), 7.16 (d, 1, J = 2.5 Hz), 7.30 (dd, 1, J = 2.6, 8.9 Hz), 7.48 (dd, 1, J = 1.6, 8.4 Hz), 7.79 (d, 1, J = 9.0 Hz), 7.84 (d, 1, J = 8.4 Hz), 8.12 (s, 1); IR (KBr pellet) 2220, 1627, 1602, 1509, 1465, 1450, 1392, 1372, 1217, 1027, 898, 830 cm^{-1}.

Demethylation of the crude material afforded 7-cyano-2-naphthol (7CN2) as a light yellow solid in 71% yield. For spectrograde material, purification by crystallization from EtOAc/hexane, followed by chromatography over silica gel using 10% EtOAc/hexane and then 20% EtOAc/hexane as eluents, yielded colorless crystals, mp 186.5−188.5 °C. Alternatively, the sublimed naphthol 7CN2, mp 185.5−186.5 °C, was purified by high-performance liquid chromatography using an Alltech column (C$_{18}$, 10 μm silica, 25 cm long, 1 cm diameter) with 10% water/90% acetonitrile as eluent. ^{1}H NMR (acetone-d_6) δ 2.85 (s, 0.2, OH), 7.38 (m, 2), 7.52, (dd, 1, J = 2.4, 8.5 Hz), 7.93 (d, 1, J = 9.5 Hz), 7.99 (d, 1, J = 8.2 Hz), 8.24 (s, 1), 9.11 (s, 0.8, OH). IR (KBr pellet) 3375, 2240, 1630, 1600, 1520, 1430, 1390, 1200, 905, 855 cm^{-1}; UV (ethanol) λ_{max} 241 nm (ϵ 58 100), 271 (5630), 281 (5470), 355 (2180). MS m/z (rel abund) M$^+$ 169 (100), 140 (38), 114 (13). Anal. Calcd for $C_{11}H_7NO$: C, 78.17; H, 4.17. Found: C, 78.10; H, 4.22.

5-Cyano-1-naphthol (5CN1). 1-Cyano-5-methoxynaphthalene was obtained in 90% yield as an orange solid using the above procedure and 5-methoxy-1-tetralone. A sample was purified by sublimation followed by crystallization from EtOAc/hexane to give colorless needles of 1-cyano-5-methoxynaphthalene: mp 88−89 °C; ^{1}H NMR (CDCl$_3$) δ 4.02 (s, 3), 6.93 (d, 1, J = 7.7 Hz), 7.49 (dd, 1, J = 7.1, 8.4 Hz), 7.61 (t, 1, J = 8 Hz), 7.80 (dd, 1, J = 1.2, 7.7 Hz), 7.90 (dd, 1, J = 1.2, 7.2 Hz), 8.51 (d, 1, J = 7.8 Hz); IR (KBr pellet) 2222, 1623, 1585, 1467, 1407, 1269, 1229, 1152, 1032, 780 cm^{-1}. Anal. Calcd for $C_{11}H_9NO$: C, 78.67; H, 4.95. Found: C, 78.80; H, 4.95.

The 1-cyano-5-methoxynaphthalene produced above was converted to 5−cyano-1-naphthol (5CN1) in 84% yield in a manner similar to that used to make 8CN2. The material was purified by chromatography over silica gel using 5% EtOAc/hexane, 10% EtOAc/hexane, and 25% EtOAc/hexane as eluents. The material was further purified by sublimation to produce 5CN2 as a light yellow powder in 75% yield: mp 202−203 °C; ^{1}H NMR (acetone-d_6) δ 3.06 (s, 0.4, OH), 7.11 (dd, 1, J = 1.2, 7.5 Hz), 7.63 (m, 3), 8.05 (dd, 1, J = 1.2, 7.1 Hz), 8.59 (d, 1, J = 8.6 Hz), 9.63 (s, 0.6, OH); IR (KBr pellet) 3320, 2236, 1621, 1584, 1406, 1374, 1278, 1140, 902, 774 cm^{-1}; UV (ethanol) λ_{max} 207 (ϵ, 48 600), 250 (38 900), 338 (4720); MS m/z (rel abund) M$^+$ 169 (100), 140 (47), 114 (20). Anal. Calcd for $C_{11}H_7NO$: C, 78.17; H, 4.17. Found: C, 78.14; H, 4.19.

5-Acetoxynaphthalene-1-sulfonyl Chloride.[21] Dimethyl formamide (0.392 g, 5.37 mmol) in 35 mL of thionyl chloride was added to the sodium salt of 5−hydroxynaphthalene-1-sulfonate (15.2 g, 55.7 mmol). The mixture was heated to 65−70 °C and stirred for 2 h. The reaction mixture was cooled and poured into 200 mL of ice. More ice was added to keep the temperature of the reaction mixture below ambient temperature. The aqueous phase was extracted with ethyl acetate (3 x 100 mL). The combined ethyl acetate phases were washed with brine (2 × 50 mL), dried (Na$_2$SO$_4$), and vacuum evaporated to yield 11.35 g (72%) of a brown solid, which was >95% pure by ^{1}H NMR spectroscopy. A sample was recrystallized from benzene: mp 127−129 °C; ^{1}H NMR (CDCl$_3$) δ 2.51 (s, 3), 7.49 (d, 1, J = 7.6 Hz),

7.65 (t, 1, J = 8Hz), 7.8 (t, 1, J = 8.2), 8.32 (d, 1, J = 8.6 Hz), 8.41, (dd, 1, J = 1.3, 7.6 Hz), 8.70 (d, 1, J = 8.8 Hz); IR (KBr) 1770, 1600, 1585, 1465, 1370, 1200, 784, 563 cm^{-1}.

1-Methoxy-5-(methanesulfonyl)naphthalene. Sodium thiosulfate (5.60 g, 44.4 mmol), sodium bicarbonate (4.52 g, 53.8 mmol), and water (250 mL) were stirred and heated to 80−90 °C. To this mixture was added 5-acetoxynaphthalene-1-sulfonyl chloride (5.00 g, 17.6 mmol) in small portions over a period of 1.5 h, and the reaction mixture was stirred for 1 h. The solution was cooled in an ice bath and acidified with 50% H$_2$SO$_4$. A precipitate formed, and the mixture was cooled for 20 min. The reaction mixture was filtered, and the solid residue was washed with cold water (3 × 5 mL). The solid material was collected and transferred to another flask. Water (15 mL) was added, and solid sodium bicarbonate (4.27 g) was carefully added over 0.5 h. Methanol (15 mL) and methyl iodide (5.0 mL, 54.0 mmol) were added to the mixture, which was refluxed with stirring overnight. The reaction mixture was poured into a 5% H$_2$SO$_4$ solution (150 mL). The resulting solid was extracted with ethyl acetate (3 × 50 mL). The combined ethyl acetate extracts were washed with water (2x) and dried, and the solvents were removed to yield 3.35 g of a brown solid. This solid was dissolved in CH$_2$Cl$_2$ and filtered through a short column of alumina using 30% EtOAc/hexanes and then CH$_2$Cl$_2$ as eluents. Evaporation of the solvents left 2.37 g (57%) of a brown solid, mp 98−101 °C. ^{1}H NMR spectroscopy showed this to be 5-(methanesulfonyl)-1-methoxynaphthalene contaminated with ca. 5% 5-(methanesulfonyl)-1-naphthol (yield 57%). The mixture was demethylated without purification in the subsequent procedure: ^{1}H NMR (CDCl$_3$) δ 3.21 (s, 3), 4.04 (s, 3), 6.96 (d, 1, J = 7.8 Hz), 7.6 (m, 2), 8.27 (d, 1, J = 8.5 Hz) 8.36 (dd, 1, J = 1.3, 7.3 Hz), 8.63 (d, 1, J = 8.5 Hz); IR (KBr pellet) 1620, 1587, 1573, 1463, 1381, 1300, 1261, 1142, 964, 774, 754 cm^{-1}; MS m/z (rel abund) M$^+$ 236 (100), 221 (8), 205 (2), 189 (3), 173 (30), 157 (35), 127 (41), 114 (17).

5-(Methanesulfonyl)-1-naphthol (5MSN1). 5-(Methanesulfonyl)-1-methoxynaphthalene (59 mg, 0.25 mmol), 48% HBr (1.0 mL) and glacial acetic acid (1.0 mL) were heated at reflux for 4 h. The solution was poured into ice, the mixture was extracted twice with EtOAc, and the combined EtOAc extracts were washed twice with water. The EtOAc solution was dried (Na$_2$SO$_4$) and purified by chromatography over silica gel using hexane (50 mL), 20% EtOAc/hexane (50 mL), and 30% EtOAc/hexane (50 mL) as eluents. Vacuum evaporation of solvents left 38 mg (0.13 mmol, 52%) of the desired (methanesulfonyl)-naphthol 5MSN1 as a colorless powder: mp 155−158 °C; ^{1}H NMR (acetone-d_6) δ 3.01 (s, 0.5, OH), 3.25 (s, 3), 7.11 (d, 1, J = 7.6 Hz), 7.58 (t, 1, J = 8 Hz), 7.67 (t, 1, J = 8 Hz), 8.22 (d, 1, J = 8.2 Hz), 8.28 (dd, 1, J = 1.4, 7.2 Hz), 8.64 (d, 1, J = 8.6 Hz), 9.58 (s, 0.5, OH); IR (KBr pellet) 3380 (br), 3020, 2921, 1625, 1590, 1572, 1460, 1290, 1272, 1130, 964, 784 cm^{-1}; UV λ_{max} 206 nm (ϵ, 39 400), 247 (33 400), 327 (4620); MS m/z (rel abund) M$^+$ 222 (100), 207 (2), 191 (2), 159 (30), 143 (29), 131 (28), 115 (71). Anal. Calcd for $C_{11}H_{10}O_3S$: 222.0351. found: 222.0350.

4-Methoxy-1,2-benzenedicarboxylic Acid.[14] The patent procedure was utilized without modification and produced the product as a colorless solid in 49% yield: ^{1}H NMR (acetone-d_6) δ 3.93 (s, 3), 7.13 (dd, 1, J = 2.7, 8.4 Hz), 7.17 (d, 1, J = 2.6 Hz), 7.87 (d, 1, J = 8.5 Hz); IR (KBr pellet) 3000 (br), 1730, 1680, 1605, 1577, 1452, 1405, 1290, 1230, 1070, 1030, 840 cm^{-1}.

1,2-Bis(hydroxymethyl)-4-methoxybenzene. Lithium aluminum hydride (4.37 g, 115 mmol) was added to 100 mL of tetrahydrofuran. The mixture was cooled with an ice bath, and 4-methoxy-1,2-benzenedicarboxylic acid (8.41 g, 42.9 mmol) in 50 mL of tetrahydrofuran was added. The bath was removed, and the mixture was heated at reflux for 2 h. The mixture was cooled in an ice bath, and water (4 mL), aqueous 15% sodium hydroxide (4 mL), and water (8 mL) were added. The solid material was removed by filtration and washed with dichloromethane, and the combined organic solutions were subjected to drying (Na$_2$SO$_4$) and vacuum evaporation to yield 6.44 g (89%) of colorless solid which was used without further purification: ^{1}H NMR (CDCl$_3$) δ 3.78 (s, 3), 4.55 (s, 2), 4.57 (s, 2), 6.77 (dd, 1, J = 2.7, 8.3 Hz), 6.86 (d, 1, J = 2.7 Hz), 7.20 (d, 1, J = 8.3 Hz); IR (thin film) 3350 (broad), 2935, 2885, 1612, 1580, 1500, 1463, 1427, 1261, 1161, 1115, 1105, 1006, 870, 822 cm^{-1}.

(21) Campbell, R. W.; Hill, H. W., Jr. *J. Org. Chem.* **1973**, *38*, 1047.

1,2-Bis[bromomethyl]-4-methoxybenzene.[14] Phosphorous tribromide (17.0 mL, 179 mmol) was added dropwise to 1,2-bis(hydroxymethyl)-4-methoxybenzene (27.0 g, 160 mmol) over a period of 6.5 h, and the mixture was stirred for an additional 12 h, cooled in a water bath, and treated with 50 mL of water. The phases were separated, and the organic phase was washed with water and saturated sodium bicarbonate solution and dried (Na_2SO_4). Removal of solvent in vacuo yielded 41.9 g of a green solid which was pure by proton NMR spectroscopy (yield 89%): mp 47−49 °C (lit.[14] 48−50 °C); ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3), 4.62 (s, 2), 4.66 (s, 2) 6.83 (dd, 1, J = 2.7, 8.5 Hz), 6.90 (d, 1, J = 2.6 Hz), 7.28 (d, 1, J = 8.4 Hz); IR (thin film) 2966, 1610, 1571, 1505, 1453, 1435, 1205, 1035, 815 cm^{-1}.

4-Methoxy-1,2-benzenediacetonitrile.[14] To finely ground KCN (22.1 g, 340 mmol) in 150 mL of Me_2SO (distilled under vacuum from CaH_2) cooled with an ice bath was added 20.7 g (70.3 mmol) of 1,2-bis(bromomethyl)-4-methoxybenzene in 50 mL of Me_2SO dropwise over 20 min. A 30 mL portion of Me_2SO was added, the mixture was stirred vigorously for 3.5 h, poured into water (1 L), and extracted with ether. The combined organic extracts were washed with 1 M HCl, saturated sodium bicarbonate solution, and water. The solution was dried (Na_2SO_4), and solvents were removed by vacuum evaporation to leave 11.9 g of a viscous brown liquid which was >90% pure by proton NMR spectroscopy. The material was used without further purification: ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 2), 3.74 (s, 2), 3.84 (s, 3), 6.90 (dd, 1, J = 2.6, 8.5 Hz), 7.00 (d, 1, J = 2.6 Hz), 7.34 (d, 1, J = 8.5 Hz); IR (thin film) 2940, 2840, 2250, 2250, 1612, 1582, 1505, 1405, 1430, 1294, 1098, 1040 cm^{-1}.

1,4-Dicyano-6-methoxynaphthalene. The method of Heiss et al. for synthesis of 1,4-dicyanonaphthalene was adapted.[22] 4-Methoxybenzene-1,2-bisacetonitrile (1.90 g, 10.2 mmol), glyoxal−bis(*tert*-butylimine) (2.26 g, 13.4 mmol), and Me_2SO (10 mL) were stirred under argon at 120 °C for 4 h. Additional bisimine (1.07 g, 6.36 mmol) was added, and the solution was stirred at 120−130 °C for 2.5 h. The material was poured hot into water (100 mL), and a precipitate formed. The solution was cooled in an ice bath and filtered. The solids were washed several times with water, dissolved in chloroform, and dried (Na_2SO_4). The solvent was removed by vacuum evaporation, and the black residue was washed with ethyl acetate (2 × 20 mL) and ethyl acetate/hexane until the residue was light brown. The filtrate was reconcentrated to form a black residue which was washed with ethyl acetate/hexane until light brown. The two portions of light brown solid were combined to yield 1.12 g (52%). This material was >95% pure by NMR spectroscopy. A sample was purified by HPLC to leave colorless prisms: mp 217−218 °C; ^{1}H NMR (CDCL$_3$) δ 4.04 (s, 3), 7.48 (dd, 1, J = 2.4, 9.2 Hz), 7.54 (d, 1, J = 2.4 Hz), 7.79 (d, 1, J = 7.5 Hz), 7.91 (d, 1, J = 7.6 Hz), 8.23 (d, 1, J = 9.2 Hz); IR (KBr pellet) 2226, 1620, 1500, 1475, 1261, 1226, 1212, 1040, 852, 829, cm^{-1}; UV (ethanol) λ_{max} 218 (ϵ, 33 500), 246 (25 800), 253 (25 800), 316 (5300), 363 (5100); MS *m/z* (rel abund) M$^+$ 208 (100), 178 (33), 165 (95), 138 (27). Anal. Calcd for $C_{13}H_8N_2O$: C, 74.99: H, 3.87; N, 13.45. Found: C, 74.84; H, 3.88; N, 13.43.

5,8-Dicyano-2-naphthol (DCN2). 1,4-Dicyano-6-methoxynaphthalene (2.11 g, 10.2 mmol), lithium iodide (3.53 g, 26.3 mmol, vacuum dried at 150 °C), and 2,4,6-collidine (20 mL) were combined and heated at 150 °C for 16 h. The hot mixture was poured into 1 M HCl solution (300 mL), and the mixture was cooled in an ice bath for 0.5 h. The precipitate was collected and washed with 1 M HCl solution and with water. The solids were dissolved in 300 mL of acetone, dried over Na_2SO_4, and concentrated in vacuo to leave 1.76 g of light brown solid that was >96% pure by ^{1}H NMR spectroscopy (yield 89%). For fluorescence spectroscopy the material was further purified by HPLC using a 25 cm x 1 cm Dynamax 60A silica column and 25% EtOAc/hexane as eluent after loading the material onto the column with 1 mL of warm tetrahydrofuran. A light yellow solid, mp 300−310 °C dec, was obtained: ^{1}H NMR (acetone-d_6) δ 7.62 (m, 2), 8.01 (d, 1, J = 7.4 Hz), 8.16 (d, 1, J = 7.4 Hz), 8.23 (d, 1, J = 8.7 Hz), 9.74 (s, 1); IR (KBr pellet) 3330, 3090, 2242, 2227, 1620, 1465, 1390, 1240, 1220, 850, 665 cm^{-1}; UV (ethanol) λ_{max} 218 (ϵ, 35 500), 246 (28 600), 319 (5100), 369 (5300); MS *m/z* (rel abund) M$^+$ 194 (100), 165 (15), 139 (19). Anal. Calcd for $C_{12}H_6N_2O$: C, 74.22; H, 3.11; N, 14.43. Found: C, 73.69; H, 3.02; N, 14.32.

(22) Heiss, L.; Paulus, E. F.; Rehling, H. *Liebigs Ann. Chem.* **1980**, 1583.

5-Hydroxy-1,2,3,4-tetrahydronaphthalene-1,4-dione. The literature procedure was followed without modification.[23] Reduction of juglone (3.14 g, 18.1 mmol), with $SnCl_2·2H_2O$ (15.1 g, 66.9 mmol) produced 2.45 g of the desired diketone in ca. 90−95% purity and 70% yield. The crude material was used without further purification: ^{1}H NMR (acetone-d_6) δ 3.08 (m,2), 3.20 (m, 2), 7.26 (dd, 1, J = 1.1, 8.3 Hz), 7.48 (dd, 1, J = 1.2, 7.3 Hz), 7.76 (t, 1, J = 8 Hz); IR (KBr pellet) 3400 (br), 1695, 1643, 1611, 1460, 1423, 1357, 1287, 1207, 1170, 810 cm^{-1}.

5,8-Dicyano-1-naphthyl Acetate. Trimethylsilyl cyanide (3.2 mL, 24 mmol) was added to dihydrojuglone (1.02 g, 5.81 mmol) and KCN/18-crown-6 catalyst (104 mg, 0.317 mmol)[24] and stirred under argon over a period of 2 min. The black solution was stirred at room temperature for 4 h, dissolved in hexane (50 mL), washed with 2% aqueous HCl solution and water, and dried (Na_2SO_4). After removal of solvent, the oily residue was dissolved in pyridine (25 mL), the solution was cooled in an ice bath, and acetyl chloride (7.0 mL, 98 mmol) was added dropwise over a period of 10 min. Chloroform (15 mL) was added, and the solution was stirred for 5 min. The ice bath was removed and the mixture heated to 90−100 °C for 1 h. A distillation head was attached to the flask, and low boiling liquids ((TMS(CN, CHCl$_3$, and acetyl chloride) were removed by distillation. The black solution was stirred at 130 °C for 2 h, cooled, and poured into ice−water (200 mL). The mixture was extracted with ethyl acetate (3 × 50 mL). The combined extracts were washed with cold 1 M HCl solution (2 × 75 mL), with saturated sodium bicarbonate, and with water. The organic extract was dried (Na_2SO_4) and concentrated to leave 1.7 g of black tar. The material was applied to a 1 × 20 column of alumina using dichloromethane and eluted with 25% EtOAc/hexane (75 mL) and 50% EtOAc/hexane (50 mL). Evaporation of solvent left a sticky orange solid (0.574 g). Some (0.467 g) of this material was purified by crystallization from hot 1:1 ethanol/methanol (20 mL). The crystals were collected by filtration and washed with methanol. Vacuum drying left 156 mg of yellow prisms, mp 147−149 °C. Water was added to the mother liquor, and more crystals formed. Filtration and drying yielded an additional 35 mg of yellow crystals (yield 13%): mp 129−139 °C; ^{1}H NMR (CDCl$_3$) δ 2.59 (s, 3), 7.55 (dd, 1, J = 1.1, 7.7 Hz), 7.85 (dd, 1, J = 7.8, 8.2 Hz), 7.99 (d, 1, J = 7.6 Hz), 8.01 (d, 1, J = 7.6 Hz), 8.28 (dd, 1, J = 1.1, 8.3 Hz); ^{13}C NMR (CDCl$_3$) δ 20.8, 110.5, 115.5, 116.1, 117.9, 123.6, 124.1, 125.6, 130.1, 131.5, 133.6. 134.5, 146.0, 169.8; IR (KBr pellet) 2235, 2218, 1776, 1617, 1574, 1461, 1375, 1194, 1128, 1023, 931, 858, 760 cm^{-1}; MS *m/z* (rel abund) M$^+$ 236 (9), 194 (100), 165 (17), 139 (14). Anal. Calcd for $C_{14}H_8N_2O_2$: C, 71.18; H, 3.41; N, 11.85. Found: C, 71.08; H, 3.41; N, 11.80.

5,8-Dicyano-1-naphthol (DCN1). 5,8-Dicyano-1-naphthyl acetate (69 mg, 0.36 mmol) was stirred for 0.5 h at room temperature in a solution of 1:1 ethanol/water (5 mL) and NaOH (161 mg). The solid gradually dissolved, and the solution turned dark red. The solution was cooled using an ice bath, a 6 N solution of HCl was added dropwise, and a precipitate formed. Water (5 mL) was added, and the solution was left at 0 °C for 0.5 h. The precipitate was collected and washed with cold water. The precipitate was washed from the funnel using acetone, and the solvent was vacuum evaporated to leave an orange powder (61 mg, 91%) that looked pure by ^{1}H NMR spectroscopy. For spectroscopy, the material was purified by sublimation (150 °C, 0.3 Torr) to leave 32 mg of light yellow prisms: mp 273−277 °C dec; ^{1}H NMR (acetone-d_6) δ 2.86 (s, 0.5, OH), 7.30 (dd, 1, J = 1.8, 7.0 Hz), 7.69 (m, 2), 8.12 (d, 1, J = 7.5 Hz), 8.20 (d, 1, J = 7.6 Hz), 10.31 (s, 0.5, OH); UV (ethanol) λ_{max} 209 (ϵ 41 000), 262 (38 100), 375 (3500); MS *m/z* (rel abund) M$^+$ 194 (100), 166 (11), 139 (33).

Fluorescence Spectra. Fluorescence spectra were recorded using a SPEX Model F112X spectrofluorometer equipped with a xenon arc lamp and single grating excitation monochromator. Sample fluorescence was collected at right angles from the excitation beam and monochromator entrance and exit slit widths were set at 1.0 nm. All spectra were corrected for the wavelength dependence of the photomultiplier response using a rhodamine B quantum counter. Data were collected every 1.0 nm.

(23) Thomson, R. H. *J. Chem. Soc.* **1950**, 1737.

(24) Evans, D. A.; Hoffman, J. M.; Truesdale, L. K. *J. Am. Chem. Soc.* **1973**, 95, 5822.

Excited-State pK_a Determination for Cyanonaphthols. Doubly distilled or deionized water was used for solution preparation. Naphthols were purified by sublimation, followed, in some cases, by crystallization or high-performance liquid chromatography, as explained above. A stock solution of $(1-2) \times 10^{-4}$ M naphthol (see Table 1) and 100–110 mg of NaOH in 100 mL of water was prepared in a volumetric flask. A portion (10.0 mL) of this was transferred to a volumetric flask containing 1.0 M NaCl solution (10.0 mL), and the flask was filled to 100 mL with water. This basic solution (pH 11.2 ± 0.1) was used as a reference to correct for variation in lamp intensity. It was observed that fluorescence from solutions at pH 11.2 did not decline significantly over a period of several hours, whereas fluorescence from solutions above pH 12 declined during the same time period. Solutions of naphthol at different pH values were made by adding 5.0 mL of naphthol stock solution to a 50 mL volumetric flask. An appropriate amount of 3.0, 0.3, or 0.03 M aqueous HCl solution was added, and the flask was filled to 50 mL with water. For solutions of dilute acid, the ionic strength was adjusted to 0.1 by adding the appropriate amount of 1.0 M NaCl solution. Solutions were prepared immediately prior to fluorescence measurement to avoid error due to decomposition of the naphthol.

Fluorescence measurements were made using 1.0 mm slit widths, except with DCN2, for which 1.0 mm slit widths were used on the excitation monochromater and 2.0 mm slit widths were used on the emission monochromater. The absorption isosbestic point in water was used as the excitation wavelength for each naphthol (Table 1).

Fluorescence Lifetimes. Excited-state lifetimes were measured at ambient temperature using a time-correlated single photon counting fluorometer which has been described previously.[25]

(25) Tolbert, L. M.; Nesselroth, S. M. *J. Phys. Chem.* **1991**, *95*, 10331.