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Solvatochromic Shifts of “Super” Photoacids

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Hydroxyarenes (ROH molecules) undergo significant enhancement in their acidity upon electronic excitation.[1,2] For example, the acidity of 2-naphthol (2N) in water increases from $\mathrm{p}K_\mathrm{a} = 9.5$ in the ground state (S_0) to $\mathrm{p}K_\mathrm{a}^* = 2.8$ in its first excited singlet state (S_1).[1] It is sufficiently acidic to transfer a proton to water during its radiative lifetime, but not to pure organic solvents. Recently, enhanced photoacids based on cyano derivatives of 2N have been synthesized and characterized.[3,4] For example, 5-cyano-2-naphthol (5CN2OH) has $\mathrm{p}K_\mathrm{a}^* \approx -1$.[5] The nearly 4 $\mathrm{p}K_\mathrm{a}$ unit difference from 2N is sufficient to allow proton transfer to an array of organic solvents, leading to the appearance of a low energy RO^- band in the fluorescence spectrum. We consider here the ROH band, which shows large solvent-induced (“solvatochromic”) spectral shifts. For example, between hexane and dimethyl sulfoxide (DMSO), it red shifts by about 3000 cm^{-1} for 5CN2OH, as compared with 1200 cm^{-1} for 2N. We focus on the origin of this large shift and its possible connection to the enhanced photoacidity.

Solvent-induced spectral shifts are usually attributed to solvent (S) polarity/polarizability effects and its hydrogen-bond (HB) donating or accepting properties. These are quantified by the empirical solvatochromic parameters of Taft and co-workers:[6,7] π^*, α, and β. In contrast, acid strength is determined by solvent basicity (its proton accepting tendency) and its dielectric properties.[8] The excited R*OH is expected to have a larger dipole moment and stronger R*OH···S bond than in the ground state. To disentangle the relative effects of β and π^* on the R*OH shifts, we compare the behavior of 5CN2OH with its methoxy analogue, 5-cyano-2-methoxynaphthalene (5CN2OMe), which is incapable of donating a HB to the solvent. Hydrogen bonding, such as in aminoarenes (HB acceptors), is known to induce mild deviations from the π^* correlation.[9,10] We demonstrate that in 5CN2OH the HB-induced bathochromic shift is substantial. Thus, specific solvation, due to hydrogen bonding, is as important as nonspecific polar solvation.

Synthesis and purification of 5CN2OH and its 5CN2OMe precursor is described elsewhere.[3,4] Solvents (Table 1) were analytical grade and did not contain fluorescent impurities. Fluorescence spectra were recorded on a SLM-AMINCO-Bowman 2 luminescence spectrometer and corrected according to manufacturer specifications. All measurements were performed at room temperature (ca. 22 °C). Sample concentrations were adjusted to optical densities of 0.05−0.1 at the excitation wavelength. Excitation spectra were independent of the emission wavelength and roughly the same as the absorption spectra in the $S_0 \rightarrow S_1$ spectral region. Likewise, emission spectra were independent of the excitation wavelength.

Table 1. Peak Emission Frequencies of the Two Cyanonaphthalene Derivatives in Different Solvents

solvent[a]	π^{*b}	β^c	$\nu_\mathrm{p}{}^d$	$\nu_\mathrm{p}{}^e$
hexane	−0.11	0	28.28	28.22
c-hexane	0	0	28.18	28.17
$\mathrm{CCl_4}$	0.21	0	27.9	27.84
$\mathrm{Et_2O}$	0.24	0.47	27.2	27.72
EtOAc	0.45	0.45	26.81	27.5
EtOH	0.54	0.77	25.89	27.3
MeOH	0.60	0.62	25.93	27.12
ACN	0.66	0.31	26.76	27.14
$\mathrm{CH_2Cl_2}$	0.73	0	27.33	27.46
$\mathrm{C_2H_4Cl_2}$	0.73	0	26.98	27.43
TFE	0.73	0	26.00	26.82
DMFA	0.88	0.69	25.38	26.86
DMSO	1	0.76	25.11	26.55
“water”	1.09	0.4[f]	25.65[g]	26.45[g]

[a] Acronyms: diethyl ether ($\mathrm{Et_2O}$), ethyl acetate (EtOAc), ethanol (EtOH), methanol (MeOH), acetonitrile (ACN), trifluoroethanol (TFE), dimethylformamide (DMFA), dimethyl sulfoxide (DMSO). [b] From ref 7. [c] From ref 6. [d] Frequency of peak 5CN2OH emission, in 1000 cm^{-1}, as obtained from a fit to the log-normal distribution.[13] [e] Same for the 5CN2OMe compound. [f] From ref 21. [g] Estimated from water/MeOH or water/ACN mixtures.

The red-edge maximum in the 5CN2OMe excitation (or absorption) spectrum exhibits a very weak bathochromic shift, from 29 300 cm^{-1} in hexane to 29 150 cm^{-1} in DMSO (not shown). This could indicate a very small ground-state dipole moment.[11] 5CN2OH exhibits a larger shift, from 29 400 cm^{-1} in hexane to 28 700 cm^{-1} in DMSO. This excess shift seems uncorrelated by the π^* polarity scale; in nonprotic solvents it increases in the order of solvent HB accepting ability, β. We conclude that a weak HB preexists in the ground electronic state,[12] contributing to 5CN2OH solvation.

A more quantitative analysis is possible from the emission spectra, Figure 1, which are sensitive to the excited-state properties. These spectra, which show sizable solvatochromic shifts, are fitted by the log-normal distribution,[13] which serves to average over the vibrational structure. From these fits (not shown), the peak frequency, ν_p, has been extracted using previously described procedures[14] (see Table 1). The shifts for 5CN2OMe emission are shown by the circles in Figure 2a. With the exclusion of the haloaliphatic compounds, they obey the correlation

$$\nu_\mathrm{p}(\mathrm{5CN2OMe}) = 28\,120 - 1520\pi^* \ (\mathrm{cm}^{-1}) \qquad (1)$$

extremely well (correlation coefficient $r = 0.996$). Thus, 5CN2OMe solvatochromism is adequately explained by polarity/polarizability effects.

In contrast, the 5CN2OH shifts (+ symbols) do not correlate well with π^*. Assuming that the dipole moments of 5CN2OMe and 5CN2OH are similar, 5CN2OMe is a good reference compound for polarity effects on 5CN2OH. Thus the excess shift,

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(1) Weller, A. *Prog. React. Kinet.* **1961**, *1*, 187.
(2) Förster, T. *Pure Appl. Chem.* **1970**, *24*, 443.
(3) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 8163.
(4) Tolbert, L. M.; Haubrich, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 10593.
(5) Huppert, D.; Tolbert, L. M.; Linares-Samaniego, S. *J. Phys. Chem. A* **1997**, *101*, 4602.
(6) Kamlet, M. J.; Abboud, J.-L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.
(7) Laurence, C.; Nicolet, P.; Dalati, M. T.; Abboud, J.-L. M.; Notario, R. *J. Phys. Chem.* **1994**, *98*, 5807.
(8) Lagowski, J. J. *Crit. Rev. Anal. Chem.* **1971**, *2*, 149.
(9) Rosenberg, H. M.; Eimutis, E. *Spectrochim. Acta* **1966**, *22*, 1751.
(10) Chapman, C. F.; Fee, R. S.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 4811.
(11) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970.
(12) Baba, H.; Suzuki, S. *J. Chem. Phys.* **1961**, *35*, 1118.
(13) Siano, D. B.; Metzler, D. E. *J. Chem. Phys.* **1969**, *51*, 1856.
(14) Agmon, N. *J. Phys. Chem.* **1990**, *94*, 2959.

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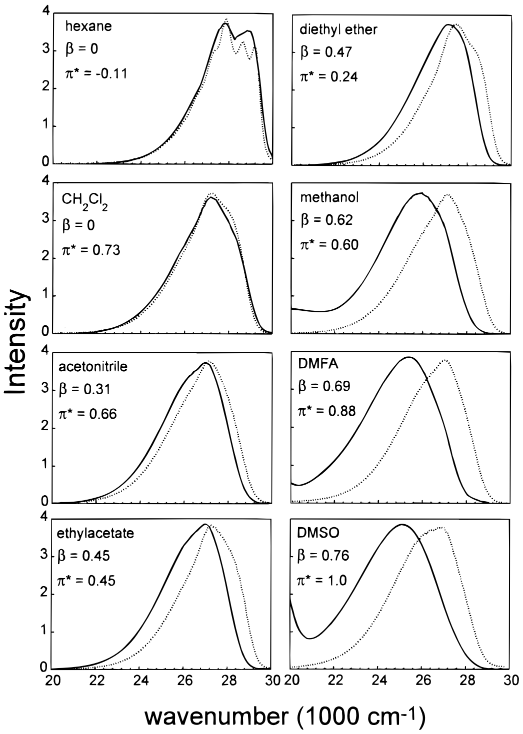

Figure 1. A comparison of 5CN2OH fluorescence emission spectra (in arbitrary intensity units) in different solvents (full lines) with those of the methoxy analogue (dashed lines).

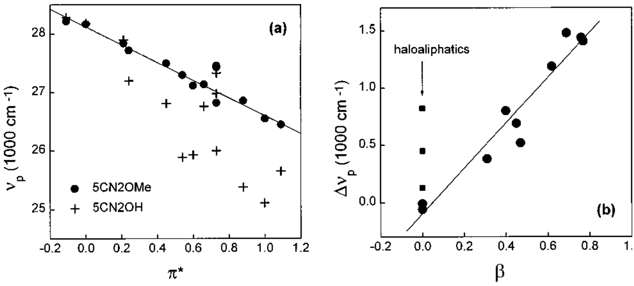

Figure 2. (a) The shift of peak R*OH emission frequency for the two cyano dyes, as obtained from a log-normal fit to the spectra in Figure 1. (b) The difference in the peak emission frequencies of the two cyano dyes correlate with β but not with π^*.

$\Delta\nu_p \equiv \nu_p(\text{5CN2OMe}) - \nu_p(\text{5CN2OH})$, reflects nonpolarity effects. Figure 2b shows that, with the exclusion of the haloaliphatics (squares), the emission data obeys

$$\Delta\nu_p = -100 + 1980\beta\ (\text{cm}^{-1}) \qquad (2)$$

with $r = 0.973$. Hence, $\Delta\nu_p$ measures the enhancement of the 5CN2OH$\cdots$**S** bond strength in the equilibrated S_1 state. Surprisingly, perhaps, the magnitude of specific solvation, due to one single HB, is comparable to that of nonspecific polar solvation. The coefficient of β (~2000 cm^{-1}) is considerably larger than what we find for the excitation spectra (~850 cm^{-1}), implying that this HB strengthens considerably in the excited state.

As an additional verification, a multilinear regression to the 5CN2OH emission data (in all 14 solvents) gives

$$\nu_p(\text{5CN2OH}) = 28\,260 - 1600\pi^* - 1950\beta\ (\text{cm}^{-1}) \qquad (3)$$

with $r = 0.990$. Indeed, the coefficients of π^* and β are nearly identical with those obtained in eqs 1 and 2, respectively, which used the methoxy derivative as a reference molecule. We do not find a dependence on α, indicating that a HB to the hydroxyl oxygen is unimportant for excited state stabilization.

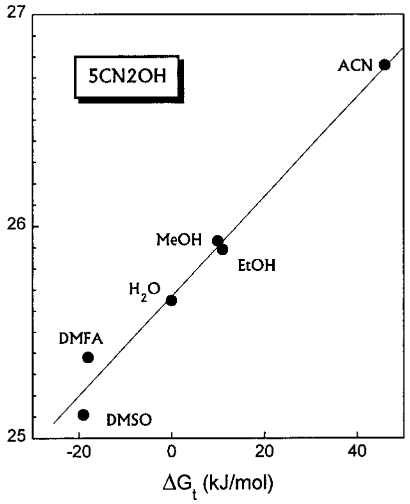

Figure 3. A correlation of the total spectral shift of the emission peak frequency of 5CN2OH, Table 1, with the free energy for transferring a proton from water to the indicated solvents. ν_p (cm^{-1}) = 25 670 + 23.5 ΔG_t (kJ/mol).

After the transfer event, the fully solvated proton is formed. Its free energy of transfer from water to various solvents, $\Delta G_t(\text{H}^+)$, has been compiled in ref 15. As Figure 3 shows, $\Delta G_t(\text{H}^+)$ correlates nicely with the *total* R*OH band shift. Proton solvation is thus dictated by the same "blend" of polarity and basicity which stabilize the excited acid (eq 3). However, the slope of the line indicates that the effect on H^+ solvation is at least three times larger than for R*OH. The ROH spectral shift is thus proportional to the free energy difference, $\Delta G_t(\text{H}^+) - \Delta G_t(\text{R*OH})$, which contributes to the acid dissociation constant.

In conclusion, our scenario for ROH excitation is as follows. Its ground state has a negligible dipole moment and a weak ROH$\cdots$S bond. When excited to S_1, both its dipole moment and its acidity increase dramatically. As a result, the HB strengthens considerably while the remaining solvent molecules rearrange to accommodate the enhanced dipole. In view of the gas-phase data[16,17] showing that, upon excitation, complexes of 1N and 2N with ammonia shorten their R*OH$\cdots$$\text{NH}_3$ bond by as much as 0.2 Å, it is likely that a similar decrease in HB length also occurs in solution. In the time domain, one might expect two ultrafast solvation phases:[10,18,19] a fast one due to HB shortening and a slower one from nonspecific solvent reorganization. In contrast, we see no evidence for a HB from protic solvents to the hydroxyl oxygen of R*OH. A more complete analysis of the excitation spectra shows that such a bond does exist in the ground state in protic solvents (HS). It must break upon excitation. Since the $\text{R*O}^-\cdots\text{HS}$ bond is crucial for anion solvation,[20] its formation could be coupled to the proton-transfer event.

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(15) Marcus, Y. *Ion Properties*; Marcel Dekker: New York, 1997.
(16) Plusquellic, D. F.; Tan, X.-Q.; Pratt, D. W. *J. Chem. Phys.* **1992**, *96*, 8026.
(17) Humphrey, S. J.; Pratt, D. W. *J. Chem. Phys.* **1996**, *104*, 8332.
(18) Prayer, C.; Gustavsson, T.; Tran-Thi, T.-H. In *Fast Elementary Processes in Chemical and Biological Systems*; Tramer, A., Ed.; AIP Conference Proceedings; American Institute of Physics: Woodbury, NY, 1996; Vol. 364, pp 333−339.
(19) Kim, S. K.; Wang, J.-K.; Zewail, A. H. *Chem. Phys. Lett.* **1994**, *228*, 369.
(20) Soumillion, J. P.; Vandereecken, P.; Van Der Auweraer, M.; De Schryver, F. C.; Schanck, A. *J. Am. Chem. Soc.* **1989**, *111*, 2217.
(21) Reichardt, C. *Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1979.