portant general classes of addition and elimination reactions. However, it is rather sobering to note that despite the wealth of quantitative data that one can obtain in such a study, the current state of knowledge allows only limited conclusions in terms of the physical significance of the magnitudes of some of the β parameters that are deduced.

Acknowledgment. We appreciate the continued support of this research by the Natural Sciences and Engineering Research Council of Canada and the award of a University of Toronto Open Fellowship to C.K.M.H.

Registry No. **1** (X = 4-$N(CH_3)_2$), 1122-58-3; **1** (X = 4-O^-), 33630-91-0; **1** (X = 3-Br, 4-O^-), 141375-46-4; **1** (X = 4-NH_2), 504-24-5; **1** (X = 4-morpholino), 2767-91-1; **1** (X = 3,5-Br_2, 4-O^-), 141375-47-5; **1** (X = 3-Br, 4-NH_2), 13534-98-0; **1** (X = 3,4-$(CH_3)_2$), 583-58-4; **1** (X = NH_2), 462-08-8; **1** (X = 3,5-$(CH_3)_2$), 591-22-0; **2** (Z = CHO), 107-02-8; **2** (Z = $COCH_3$), 78-94-4; **2** (Z = SO_2CH_3), 3680-02-2; **2** (Z = $C_5H_4NCH_3$), 45708-76-7; **2** (Z = CO_2CH_3), 96-33-3; **2** (Z = $CONH_2$), 79-06-1; **2** (Z = $CON(CH_3)_2$), 2680-03-7; **3** (X = 4-$N(CH_3)_2$, Z = $COCH_3$), 141375-39-5; **3** (X = 4-$N(CH_3)_2$, Z = SO_2CH_3), 141375-40-8; **3** (X = 4-$N(CH_3)_2$, Z = CHO), 141375-38-4; **3** (X = 4-$N(CH_3)_2$, Z = $CONH_2$), 141375-42-0; **3** (X = 4-$N(CH_3)_2$, Z = $CON(CH_3)_2$), 141375-43-1; **3** (X = 4-$N(CH_3)_2$, Z = $C_6H_4NCH_3$), 141375-41-9; **3** (X = 4-O^-, Z = CHO), 141375-48-6; **3** (X = 3-Br, 4-O^-, Z = CHO), 141375-49-7; **3** (X = 4-NH_2, Z = CHO), 141375-50-0; **3** (X = 4-morpholino, Z = CHO), 141375-51-1; **3** (X = 3,5-Br_2, 4-O^-, Z = CHO), 141375-52-2; **3** (X = 3-Br, 4-NH_2, Z = CHO), 141375-53-3; **3** (X = 3,4-$(CH_3)_2$, Z = CHO), 141375-54-4; **3** (X = 3-NH_2, Z = CHO), 141375-55-5; **3** (X = 4-O^-, Z = $COCH_3$), 68634-57-1; **3** (X = 3-Br, 4-O^-, Z = $COCH_3$), 141375-56-6; **3** (X = 4-NH_2, Z = $COCH_3$), 141375-57-7; **3** (X = 4-morpholino, Z = $COCH_3$), 141375-58-8; **3** (X = 3,5-Br_2, 4-O^-, Z = $COCH_3$), 141375-59-9; **3** (X = 3-Br, 4-NH_2, Z = $COCH_3$), 141375-60-2; **3** (X = 3,4-$(CH_3)_2$, Z = $COCH_3$), 141375-61-3; **3** (X = 3,5-$(CH_3)_2$, Z = $COCH_3$), 141375-62-4; **3** (X = NH_2, Z = $COCH_3$), 141375-63-5; **3** (X = 3-Br, 4-O^-, Z = SO_2CH_3), 141375-64-6; **3** (X = 4-NH_2, Z = SO_2CH_3), 141375-65-7; **3** (X = 4-morpholino, Z = SO_2CH_3), 141375-66-8; **3** (X = 3,5-Br_2, 4-O^-, Z = SO_2CH_3), 141375-67-9; **3** (X = 3-Br, 4-NH_2, Z = SO_2CH_3), 141375-68-0; **3** (X = 3,4-$(CH_3)_2$, Z = SO_2CH_3), 141375-69-1; **3** (X = 3,5-$(CH_3)_2$, Z = SO_2CH_3), 141375-70-4; **3** (X = 3-NH_2, Z = SO_2CH_3), 141375-71-5; **3** (X = 3-Br, 4-O^-, Z = $CONH_2$), 141375-72-6; **3** (X = 4-NH_2, Z = $CONH_2$), 141375-73-7; **3** (X = morpholino, Z = $CONH_2$), 141375-74-8; **3** (X = 3,5-Br_2, 4-O^-, Z = $CONH_2$), 141375-75-9; **3** (X = 3-Br, 4-NH_2, Z = $CONH_2$), 141375-76-0; **5**, 141375-78-2; **6**·Br, 141375-77-1; (*E*)-$CH_3CH{=}CHCHO$, 123-73-9; $CH_2{=}C(CH_3)CHO$, 78-85-3; 2-(2-bromomethyl)-1,3-dioxane, 33884-43-4; 3-(4-(dimethylamino)pyridinium)butanal, 141375-44-2; 2-methyl-3-(4-(dimethylamino)pyridinium)propanal, 141375-45-3.

Supplementary Material Available: Experimental conditions for the individual kinetic studies of all **1** with all **2** (Tables S1 and S2) and proton-decoupled ^{13}C NMR spectra referred to in the Experimental Section (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from ACS; see any current masthead page for ordering information.

Hydrogen Bonding between a *N*-Pyridinium Phenolate Betaine and O–H Donors in Acetonitrile

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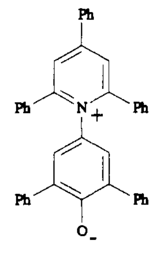
Hydrogen bonding between 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenolate (1, Dimroth's dye) and water, alcohols, and phenols has been measured spectrophotometrically in acetonitrile at 25 °C. Association constants for 1:1 hydrogen-bonded complexes range from $K_{AB} = 2\ M^{-1}$ for water to $K_{AB} = 6.06 \times 10^3\ M^{-1}$ for *m*-nitrophenol with a Brønsted slope $\alpha = 0.38 \pm 0.04$ for substituted phenols with $pK_a > 23$. The acidity constant of 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenol was determined by potentiometric titration: $pK_a = 22.1 \pm 0.2$. Hydrogen bonding of phenols is analyzed within the framework of the Hine equation that describes changes in the strength of the hydrogen bond with changes in the pK_a of the hydrogen-bond donor and acceptor. A value of the Hine interaction coefficient $\tau = 0.016 \pm 0.002$ is consistent with a double-minimum potential for the ArOH···1 hydrogen bond.

Introduction

Since the early classification of solvents as "protic" and "aprotic" by Brønsted[1] there have been many attempts to provide a quantitative description of solvent polarity. One of the most widely used scales of solvent polarity is the $E_T(30)$ scale. This scale is based on the increases in the wavelength of the charge-transfer absorption band of 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenolate, **1**, in nonpolar solvents that correspond to decreases in $E_T(30)$ values.[2,3]



1

For example, the absorption maximum of **1** shifts from 453 nm in water to 627 nm in the polar aprotic solvent acetonitrile, with even larger shifts for more nonpolar solvents. These solvent-induced shifts, termed "solvatochromism", are caused by changes in the interac-

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[1] Brønsted, J. N. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 2049.

[2] Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; Verlag Chemie: Weinheim, 1988.

[3] Johnson, B. P.; Gabrielsen, B.; Matulenko, M.; Dorsey, J. G.; Reichardt, C. *Anal. Lett.* **1986**, *19*, 939.

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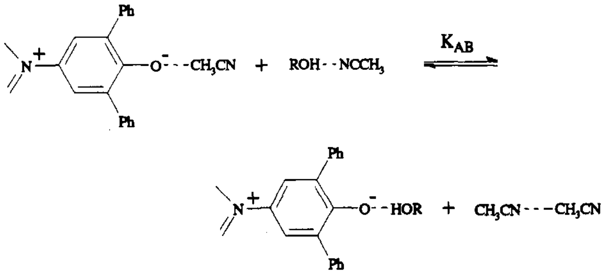
tions between *N*-pyridinium phenolate betaines and the solvent in the ground state and excited state of the dye.

The possibility that the absorption spectra of *N*-pyridinium phenolate betaines will be perturbed by specific hydrogen-bonding interactions with proton donors is often suggested[4-10] but there are few direct spectroscopic studies of this phenomenon.[4,5,10] The demonstration of nonlinear increases in $E_T(30)$ values with increasing mole fraction of hydrogen-bond-donor solvents in binary solvent mixtures provides indirect evidence for hydrogen bonding between the betaine dye and hydrogen-bond donors.[11-13]

Hydrogen-bonding interactions between a hydrogen-bond donor and the phenolate oxygen will lead to a stabilization of its ground state relative to the less-polar excited state,[2,6] and this will be accompanied by a decrease in the wavelength of the absorption maximum that corresponds to an increase in the observed $E_T(30)$ value. Thus, empirical measures of solvent polarity like the E_T(30) scale may not provide a useful description of macroscopic properties when specific molecular interactions like hydrogen bonding occur.[4,5] We report here evidence that 1 forms hydrogen bonds with dilute solutions of proton donors such as alcohols (eq 1), phenols, and water that increase in strength with increasing acidity of the proton donor in acetonitrile. These results provide quantitative support for suggestions[5-8] that the $E_T(30)$ scale is at least as much a measure of solvent hydrogen-bond-donor ability as it is of solvent polarity in protic solvents. The data for hydrogen bonding of phenols allow an estimate of the Hine interaction coefficient, $\tau = 0.016$, that describes changes in the strength of the hydrogen bond with changes in the pK_a of the hydrogen-bond donor and acceptor in acetonitrile.



(1)

Experimental Section

Materials. 4-(2,4,6-Triphenylpyridinio)-2,6-diphenylphenolate, 1, was obtained as a gift from Professor N. Pienta or purchased from Aldrich. The dye was recrystallized from 3:1 (v/v) methanol/water and dried in vacuo over P_2O_5.[3] Substituted phenols were recrystallized, sublimed, or distilled before use. Reagent-grade inorganic salts were used without further purification. Fisher HPLC-grade acetonitrile containing 2 ppm water was used without further purification. The solvent was free of acidic impurities as shown by the absence of any spectral shifts of 1 in the presence of 1 mM sodium methoxide. Absorption spectra were measured using Hitachi U-2000 (resolution: ±0.2 nm), Cary 210 (resolution: ±0.25 nm), or Hewlett-Packard 8452A (resolution: ±1 nm) spectrophotometers in tightly stoppered 1- or 10-cm cells at 25 °C.

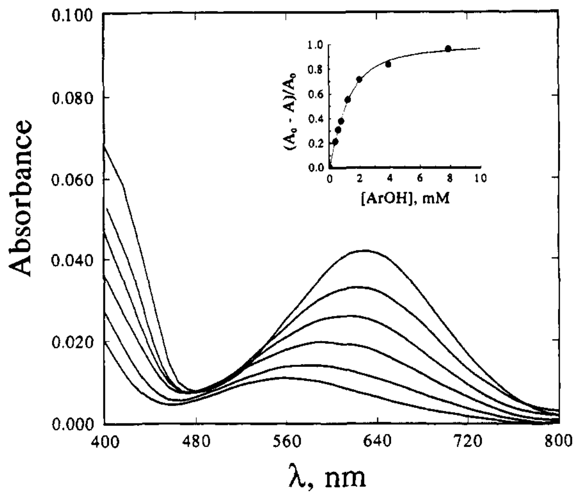


Figure 1. Spectral changes of 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenolate, 1, in the presence of *p*-bromophenol in acetonitrile. Inset: plot of the relative decrease in absorbance at 626 nm as a function of increasing *p*-bromophenol concentration. The data fit to eq 3 with K_{AB} = 823 M^{-1}, K_{A_2B} = 5670 M^{-2}, and ϵ_{AB}/ϵ_B = 0.27.

Methods. Acidity constants for substituted phenols, including 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenol, were determined by potentiometric titration using a Metrohm EA 121 glass electrode as described by Beltrame et al.[14] and Kolthoff et al.[15] A constant electrode potential was usually attained within 3–5 min. The reference potential E^0 = 1040 ± 3 mV was checked periodically using picric acid (pK_a = 11.00) as a standard. The pK_a values for substituted phenols were within ±0.2 pK units of literature values.[16] Potentiometric titrations of 4–7 mM dye with 0.7 M $HClO_4$ yielded linear slopes of relative potential against log ([1**H**]/[1]) equal to 60.2 ± 2.6 mV in the range 10 > [1**H**]/[1] > 0.2. The addition of small quantities of water (<200 ppm) was shown to have no effect on the measured potential.[14] The data are summarized in Table S1 of the supplementary material.[17]

Results

The visible spectrum of 1 in the presence of increasing concentrations of hydrogen-bond donors such as water,[12,18] alcohols,[13] and substituted phenols shows a steady decrease in the intensity of the $\pi \rightarrow \pi^*$ charge-transfer band at 627 nm in acetonitrile. There is a parallel increase in the weaker band at 520–550 nm that can be assigned to the hydrogen-bonded betaine, ROH⋯1. Figure 1 shows the decrease in the absorbance of the dye in the presence of increasing concentrations of *p*-bromophenol. At high proton-donor concentrations a further hypsochromic shift occurs in the absorption spectrum, with loss of an apparent isosbestic point.[19] This is consistent with the formation of higher order complexes of the type 1⋯$(HA)_n$ with n = 1, 2, or 3.[20-23]

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Table I. Association Constants for Hydrogen Bonding between 4-(2,4,6-Triphenylpyridinio)-2,6-diphenylphenolate and O–H Donors in Acetonitrile at 25 °C

X–OH	pK_a[a]	10^{-2} K_{AB},[b] M^{-1}	10^{-3} K_{A_2B},[b] M^{-2}	ϵ_{AB}/ϵ_B
H_2O		0.02 ± 0.001	0.001 ± 0.0004	0.65
ethanol		0.05 ± 0.015	0.002 ± 0.001	0.62
trifluoroethanol		4.64 ± 1.3	3.48 ± 1.3	0.65
2,6-di-*tert*-butyl-4-methylphenol		<0.0004		
p-methoxyphenol	(28.0)[c]	2.35 ± 0.07	4.02 ± 0.12	0.50
phenol	(27.2)[c]	2.74 ± 0.4	6.27 ± 0.29	0.43
p-bromophenol	25.8 (25.6)[c]	8.23 ± 1.6	5.67 ± 3.5	0.27
m-trifluorocresol	25.1 (24.9)[c]	22.0 ± 3	309 ± 25	0.05
m-cyanophenol	24.6	48.6 ± 3	9550 ± 990	0
m-nitrophenol	23.9 (23.85)[c]	60.6 ± 5	*d*	0
p-nitrophenol	21.3 (20.9)[c]	*e*		

[a] pK_a values were determined potentiometrically as described in the Experimental Section and have uncertainties of <±0.2. [b] Values of K_{AB} and K_{A_2B} defined by eq 2 were obtained according to eq 3 at 626 nm. [c] Chantooni, M. K., Jr.; Kolthoff, I. M. *J. Phys. Chem.* **1976**, *80*, 1306. [d] The data were fit with a single hydrogen-bonding association constant. [e] No absorption at λ > 500 nm.

Association constants for formation of *n*:1 hydrogen-bonded complexes can be described by eq 2:

$$B + nAH \xrightleftharpoons{K_{A_nB}} (AH)_nB \qquad (2)$$

Association constants were determined by measuring the decrease in the absorbance of the charge-transfer band in the presence of increasing concentrations of alcohols, water, and substituted phenols. Association constants K_{AB} for formation of 1:1 complexes and K_{A_2B} for formation of 2:1 complexes were obtained from fitting the data according to eq 3 using a nonlinear least-squares fitting routine.[25]

$$\frac{A_o - A}{A_o} = \frac{(1 - \epsilon_{AB}/\epsilon_B)K_{AB}[AH] + (1 - \epsilon_{A_2B}/\epsilon_B)K_{A_2B}[AH]^2}{1 + K_{AB}[AH] + K_{A_2B}[AH]^2} \qquad (3)$$

where A and A_o are the absorbance of the long-wavelength charge-transfer band of 1 at 626 nm in the presence and absence of the proton donor, ϵ_{AB} and ϵ_{A_2B} are the extinction coefficients for the hydrogen-bonded species, AH···1 and $(AH)_2$···1, and $\epsilon_B = 4.9 \times 10^3$ M^{-1} cm^{-1} is the extinction coefficient for 1.[18] For each concentration of 1, 6–15 solutions of the alcohol or phenol were used with [AH] > [1] and the ratio of extinction coefficients $\epsilon_{A_2B}/\epsilon_B$ was assumed to be zero. Because of the availability of three lone pairs on the phenolate oxygen of 1 there is also the possibility of forming 3:1 complexes between the dye and various proton donors. However, no significant improvement in the fit of the experimental data to a function describing formation of 3:1 complexes was observed. Association constants $K_{AB} = 8.23 \times 10^2$ M^{-1} and $K_{A_2B} = 5.67 \times 10^3$ M^{-2} for *p*-bromophenol were obtained from a fit of the absorbance at 626 nm in Figure 1 to eq 4.

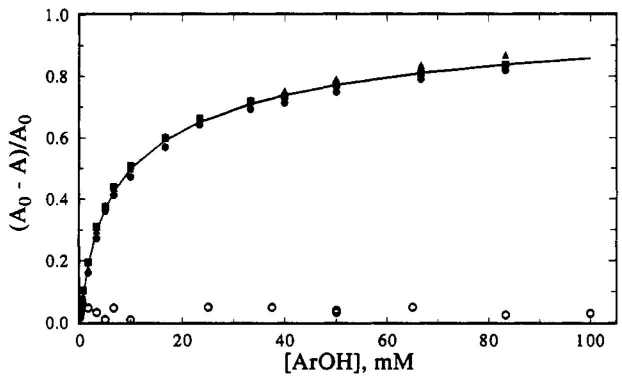

Figure 2. Relative change in absorbance of 1 at 626 nm with increasing concentration of phenol (filled symbols) and 2,6-di-*tert*-butyl-4-methylphenol (open symbols) in acetonitrile: [1] = 0.08 mM (●), 0.17 mM (■), and 0.25 mM (▲). The solid line is a nonlinear least-squares fit of the data to eq 3 with K_{AB} = 274 M^{-1}, K_{A_2B} = 6270 M^{-2}, and ϵ_{AB}/ϵ_B = 0.43.

Figure 2 shows that 1:1 hydrogen bonding is weaker for phenol with $K_{AB} = 2.35 \times 10^2$ M^{-1}. The sterically hindered 2,6-di-*tert*-butyl-4-methylphenol shows no evidence of hydrogen-bond formation up to a concentration of 100 mM. The data for phenol were obtained at several different dye concentrations and show that the hydrogen-bonding association constant is essentially independent of [1]. Although the absorption maxima at 520–550 nm for the hydrogen-bonded complexes ROH···1 are very broad, there is no significant change in the position of this broad band with changes in the acidity of the phenols with pK_a > 23. In the presence of substituted phenols or ammonium ions with pK_a < 22, however, this weak band is lost entirely and there is no significant absorbance greater than 500 nm, even at low concentrations of the alcohol or ammonium ion (data not shown).

Table I summarizes association constants K_{AB} and K_{A_2B} for hydrogen bonding between 1 and several proton donors including H_2O, alcohols, and substituted phenols. Also included in Table I are pK_a values for several substituted phenols determined potentiometrically as described in the Experimental Section. The pK_a = 22.1 ± 0.2 for the conjugate acid of 1 was also determined by potentiometric titration with perchloric acid.

Discussion

The data in Figures 1 and 2 and Table I show that 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenolate forms hydrogen bonds that depend upon the acidity and steric hindrance of the proton donor. These results are not consistent with a nonspecific solvent effect. Such an effect would not be expected to show the saturation behavior of eq 3.[4] The absence of any significant change in the absorption spectra of 1 in the presence of up to 100 mM 2,6-di-*tert*-butyl-4-methylphenol is consistent with the fact that the bulky *tert*-butyl groups lengthen the hydrogen bond and eliminate any significant stabilization of the ground state of 1 by hydrogen bonding. Further evidence

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(23) In the case of water acting as a hydrogen-bond donor, the small change in the isosbestic point at 462 nm at $[H_2O] \sim 0.8$ M (Table S2; Figure S1)[17] is consistent with the formation of higher order complexes of water, as suggested by Muney and Coettzee on the basis of changes in the molar absorbtivity at 1410 nm of the first overtone of water in acetonitrile.[24]

(24) Muney, W. S.; Coetzee, J. F. *J. Phys. Chem.* **1962**, *66*, 89.

(25) The data were fit using Enzfitter by Biosoft software (J. Leatherbarrow, Elsevier, New York, 1987) using the equations derived in the Appendix.[17] See also: Hogfeldt, E. In *Treatise on Analytical Chemistry*, 2nd Ed.; Kolthoff, I. M., Elving, P. J., Eds.; Wiley-Interscience: New York, 1979; Part 1, Vol. 2, pp 25–26.

that 1 forms specific hydrogen bonds with proton donors comes from the increase in hydrogen-bond association constants K_{AB} with increasing acidity of substituted phenols (Table I) as well as the complete absence of the long-wavelength absorbance band for acids with a $pK_a < 22$. With stronger acids, proton transfer across the hydrogen bond is thermodynamically favorable based upon the measured $pK_a = 22.1$ for 1–H Thus complete proton transfer to the phenolate oxygen of 1 to form the ion-pair intermediate 1–H$\cdots{}^{-}$A occurs.

The observation of specific hydrogen bonding effects on the absorption spectra of 1 confirms and extends the view that the $E_T(30)$ solvent polarity scale reflects the solvent hydrogen-bond-donor ability as well as its overall solvent polarity.[5–9] For example, the anomalously large $E_T(30)$ values for organic molten salts containing N–H proton donors have been interpreted as evidence for specific hydrogen-bond-donor effects.[9] Kamlet, Abboud, and Taft[7] have demonstrated a multiple linear regression correlation that relates their scale of solvent polarity–polarizability (π^*) and solvent hydrogen-bond-donor acidities (α_{sol}) with the $E_T(30)$ scale as described in eq 4.

$$E_T(30) = 16.3\pi^* + 15.8\alpha_{sol} + 29.35 \text{ kcal mol}^{-1} \quad (4)$$

In eq 4, the Kamlet and Taft α_{sol} values describe solvent hydrogen-bond-donor acidities in neat solvents and are not to be confused with the Brønsted α coefficient that describes the sensitivity of values of log K_{AB} to the acidity of the hydrogen-bond-donor solutes in dilute solution described below. The relative ratio of the π^* and α_{sol} coefficients close to one shows that both properties contribute about equally to the solvatochromic behavior of 1 in neat solvents.

As pointed out by Taft and Kamlet,[5] eq 4 describes hydrogen-bonding effects in neat, strongly self-associated solvents and there is no a priori reason to expect similar orderings of hydrogen-bond-donor strengths of R–OH in dilute solutions. This is confirmed by the small change in the hydrogen-bond association constants K_{AB} for ethanol relative to water despite different α_{sol} values of 0.86 and 1.17 for ethanol and water, respectively.[26] In this context it is also interesting to note that acetonitrile is a surprisingly good hydrogen-bond-donor solvent according to the α_{sol} scale proposed by Taft and Kamlet.[5,7] For example, typical α_{sol} values for aliphatic alcohols range from $\alpha_{sol} = 0.79$ for *n*-butanol to $\alpha_{sol} = 1.51$ for trifluoroethanol, whereas the α_{sol} value equal to 0.19 for acetonitrile[26] is correspondingly smaller. The smaller α_{sol} value suggests that the self-association complexes of the type $CH_3CN\cdots H_3CCN$ indicated on the right-hand side of eq 1 are weak, but not negligible, in acetonitrile solvent.

Application of the Hine Equation To Describe Hydrogen Bonding in Acetonitrile. The strength of a hydrogen bond between *dilute* solute acids AH and bases B in any solvent SH depends upon the differences in the solute–solvent interactions (AH$\cdots$SH and SH$\cdots$B) and the sum of the interactions across the AH$\cdots$B hydrogen bond and any solvent–solvent hydrogen-bond interactions (S-H$\cdots$SH) as described by eq 5. The energetics of eq 5 can

$$\text{AH}\cdots\text{SH} + \text{SH}\cdots\text{B} \xrightleftharpoons{K_{AB}} \text{AH}\cdots\text{B} + \text{SH}\cdots\text{SH} \quad (5)$$

be quite complex, especially when AH or B are charged species. Insight into the nature of the energetics described by eq 5 can be obtained from a very simple approach of varying the acidities, pK_a^{AH} and pK_a^{BH}, of the hydrogen-bond donor AH or acceptor B, respectively. In the case where the acids and/or bases are part of a structurally homogenous series, the hydrogen-bond association constants K_{AB} will follow Brønsted correlations with slopes $\alpha = \partial \log K_{AB}/{-\partial}pK_a^{AH}$ and $\beta = \partial \log K_{AB}/\partial pK_a^{BH}$, respectively. The magnitude of these coefficients will be significantly less than 1 in cases where no ion pairs, $A^{-}\cdots{}^{+}HB$ are formed from proton transfer across the hydrogen bond.[27]

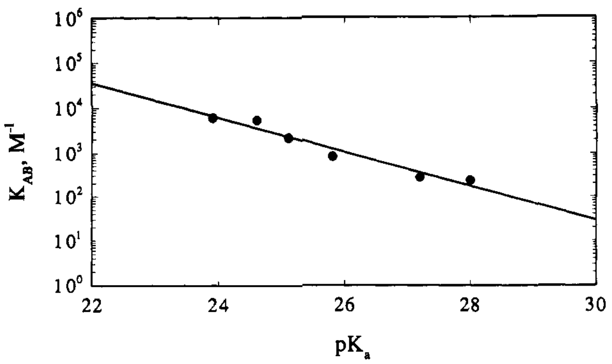

Figure 3. Brønsted plot for the formation of 1:1 hydrogen-bonded complexes of substituted phenols with 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenolate, 1, in acetonitrile. The line has a slope $\alpha = 0.38 \pm 0.04$ that is a least-squares fit to the experimental points.

The Brønsted coefficients α and β are related to each other, as discussed by Hine.[28] Following the expression derived by Hine that describes hydrogen bonding in hydroxylic solvents, hydrogen bonding in acetonitrile can be described by eq 6 where pK_{SH} and $pK_{SH_2^+}$ refer to the

$$\log K_{AB} = \tau(pK_a^{AH} - pK_{SH})(pK_{SH_2^+} - pK_a^{BH}) - \log(\chi\cdot[\text{SH}]) \quad (6)$$

ionization of the solvent species CH_3CN and CH_3CNH^+, respectively,[29] τ is an interaction coefficient that describes the change in the strength of the hydrogen bond with changes in the pK_a of the proton donor and acceptor, and χ is an empirical constant, or "statistical factor", that describes the ability of acetonitrile to share a proton in a solvent–solvent hydrogen bond, as described in more detail below. The Hine interaction coefficient τ is related to the Brønsted coefficients α and β by eqs 7 and 8.

$$\alpha = -\tau(pK_{SH_2^+} - pK_a^{BH}) \quad (7)$$

$$\beta = -\tau(pK_a^{AH} - pK_{SH}) \quad (8)$$

Figure 3 shows that hydrogen bonding between 4-(2,4,6-triphenylpyridinio)-2,6-diphenylphenolate with $pK_a^{BH} = 22.1$ and substituted phenols with $pK_a^{AH} > 23$ follows a Brønsted correlation with a slope of $\alpha = 0.38 \pm 0.04$. The data in Figure 3 are consistent with a value of $\tau = 0.016 \pm 0.002$ calculated according eq 6 using a value of $\chi = 3 \times 0.19$, or more directly from eq 7, without any assumptions regarding a value of χ.[32]

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[29] The solvent acidity constants K_{SH} and $K_{SH_2^+}$ are derived from the concentration of acetonitrile in neat solvent (24.4 M) and the autoprotolysis constant ($pK_{auto} = 33.6$) of acetonitrile[30,31] according to $K_{SH_2^+} = 1/[CH_3CN]$ and $pK_{SH} = pK_{auto} + \log[CH_3CN]$.

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The small amount of available data on hydrogen bonding in acetonitrile suggests that the value of $\tau = 0.016$ for hydrogen bonding of 1 to phenols is reasonable. It is similar to values of $\tau = 0.017$ for hydrogen bonding of Cl^- to phenols[33] and $\tau = 0.017$ for formation of *p*-BrPhOH$\cdots{}^-$OAr hydrogen bonds in acetonitrile.[34] An upper limit for $\tau < 0.027$ in acetonitrile can be derived from eq 6 assuming that the concentration of the hydrogen-bonded pair $CH_3CNH^+\cdots{}^-NCCH_2$ cannot exceed the concentration of CH_3CN in liquid acetonitrile, i.e., $K_{AB} < [CH_3CNH^+\cdots{}^-NCCH_2]/([CH_3CNH^+][CH_2CN^-]) < 24.4/K_{auto} = 10^{35}$ M^{-1} where $pK_{auto} = 33.6$.[30,31] Using eq 6, this leads to a maximum value of $\tau < 0.027$ and corresponds to the movement of a proton between the acid and base sites in a single minimum potential. If there are two potential minima, then τ may be seen to be less than 0.027.[28] This suggests that a smaller value of τ for the complex ArOH$\cdots$1 is consistent with steric interactions that increase the distance across the hydrogen bond and decrease the electrostatic interaction between the acid and base.

The Hine equation was originally derived for electrostatic interactions across a neutral O–H$\cdots$O hydrogen bond in hydroxylic solvents so it is perhaps surprising that it can be extended to charged hydrogen bonds in nonhydroxylic solvents. The Hine equation has been used to describe the behavior of O–H$\cdots{}^-$O and N–H$^+\cdots{}^-$O hydrogen bonds in water at ionic strength 2 M with $\tau = 0.013$.[35] Bernasconi et al.[36] have measured $\tau = 0.028$ for N–H$^+\cdots{}^-$O hydrogen bonds in 90% Me_2SO–10% water solution. Hine[28] has noted that hydrogen bonding in CCl_4 shows behavior consistent with eq 7. For example, the slopes of linear free energy relationships between log K_f for hydrogen-bond formation between neutral bases and O–H acids versus log K_f values for hydrogen-bond formation between *p*-fluorophenol and the corresponding bases *increase* for more acidic O–H acids in CCl_4.[27] This shows that there is an increase in the sensitivity of hydrogen-bond strength to increases in the acidity of the O–H acid. This is consistent with a positive value of τ in CCl_4.

The small value of τ and the absorption maxima for the hydrogen-bonded complexes ArOH$\cdots$1 that are essentially independent of the pK_a of the acid ArOH are consistent with movement of a proton in a double-minimum potential in which the proton is covalently bonded to the acid ArOH with a barrier for transfer of the proton across the hydrogen bond. Similar conclusions have been reached on the basis of changes in the electronic spectra of hydrogen bonded complexes of the type OH$\cdots{}^-$O with changes in the acidity of the hydrogen-bond donor in sulfolane and acetonitrile.[37,38] Band-shape analysis of the charge-transfer band of 2,4,6-triphenyl-*N*-(3,5-di-*tert*-butyl-4-hydroxyphenyl)pyridinium ion in proton-donor solvents provides further evidence for hydrogen bonding of *N*-pyridinium phenolates.[10] Changes in the shape of the spectrum of this betaine dye upon going from polar aprotic solvents to alcohol solvents have been interpreted as evidence for coupling of high-frequency nuclear modes, due to reorganization of the C–N and C–O framework upon excitation, with O–H stretching and bending modes of the solvent. The small 200 cm^{-1} decrease in methanol-*O*-*d* of the molecular vibrational frequency at 2400 cm^{-1} assigned to the hydrogen-bonded $CH_3OH\cdots{}^-O$ stretch is consistent with the expected strongly unsymmetrical hydrogen bond that gives rise to a fractionation factor close to unity.[38]

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Registry No. 1, 10081-39-7; H_2O, 7732-18-5; ethanol, 64-17-5; trifluoroethanol, 75-89-8; 2,6-di-*tert*-butyl-4-methylphenol, 128-37-0; *p*-methoxyphenol, 150-76-5; phenol, 108-95-2; *p*-bromophenol, 106-41-2; *m*-trifluorocresol, 98-17-9; *m*-cyanophenol, 873-62-1; *m*-nitrophenol, 554-84-7; *p*-nitrophenol, 100-02-7.

Supplementary Material Available: Potentiometric titration data for 1, absorbance versus phenol and water concentration data, Tables S1–S3, Figure S1, and the derivation of eq 3 (6 pages). Ordering information is given on any current masthead page.

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(32) Equation 6 differs from the equation proposed by Hine in the constant on the right-hand side of eq 6. To a first approximation χ should be related to Taft and Kamlet's α_{sol} value that describes the ability of the solvent to act has a hydrogen-bond donor,[5,26] modified by a statistical factor of 3 that reflects the possibility of forming a hydrogen bond with each of the C–H bonds of acetonitrile. In hydroxylic solvents $\chi = 1$, consistent with the strong self-association in these solvents. A smaller value is expected in acetonitrile reflecting the fact that not all possible $H_3CCN\cdots H_3CCN$ hydrogen bonds are formed from self-association of the solvent. The value of $\chi = 0.19$ needed to fit the data in Figure 3 is in good agreement with the "best" $\alpha_{sol} = 0.19$ ● 0.08 reported by Kamlet et al.[26] Although the value of the constant on the right hand side of eq 6 seems reasonable, in the final analysis its exact value must be considered on its ability to fit the experimental data.

(33) The value of $\tau = 0.017 = -0.20/(pK_{SH_2^+} - pK_a^{HCl})$ is calculated from a rearranged form of eq 7 using data for hydrogen-bond association constants $K^f_{HACl^-}$ for substituted phenols[16] with $\alpha = \rho/\rho_{eq} = 0.99/4.76 = 0.20$ and $pK_a^{HCl} = 10.4$ (ref 30).

(34) The value of $\tau = 0.017 = -0.17/(pK_a^{AH} - pK_{SH})$ for hydrogen bonding of *p*-BrPhOH$\cdots{}^-$OAr is calculated from a rearranged form of eq 8 using data for hydrogen-bond association constants $K^f_{HRA^-}$ for meta-substituted phenols[16] with $\beta = \rho/\rho_{eq} = 0.79/4.76 = 0.17$ and $pK_a^{AH} = 25.8$ for *p*-bromophenol.

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