

## Linear Solvation Energy Relationships. 23. A Comprehensive Collection of the Solvatochromic Parameters, $\pi^*$ , $\alpha$ , and $\beta$ , and Some Methods for Simplifying the Generalized Solvatochromic Equation

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The solvatochromic parameters are intended for use in linear solvation energy relationships (or, in the case of solute/solute interactions, linear complexation energy relationships) of the generalized form  $XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H + e\xi$ . This equation may be reduced to a more manageable form by a judicious choice of solvents and reactants or indicators. One-, two-, and three-parameter correlations involving different combinations of the above parameters and various types of physicochemical properties are demonstrated. A comprehensive and up-to-date collection of  $\pi^*$ ,  $\alpha$ , and  $\beta$  values is presented.

The present paper demonstrates how the *solvatochromic comparison method* may be used to unravel, quantify, correlate and rationalize multiple interacting solvent effects on many types of physicochemical properties and reactivity parameters. A further purpose is to assemble in one convenient reference an up-to-date (as of Feb 1983) and comprehensive collection of the solvatochromic parameters  $\pi^*$ ,  $\alpha$ , and  $\beta$ . The  $\pi^*$  scale is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect.<sup>1-4</sup> Values of  $\pi^*$  for "select solvents", nonchlorinated nonprotonic aliphatic solvents with a single dominant bond dipole, have been shown to be generally proportional to molecular dipole moments.<sup>4</sup> The  $\alpha$  scale of solvent HBD (hydrogen-bond donor) acidities describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond.<sup>1,5-7</sup> The  $\beta$  scale of HBA (hydrogen-bond acceptor) basicities provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond.<sup>1,8-11</sup> The  $\beta$  scale has also been used to evaluate hydrogen-bond-acceptor strengths of solid HBA bases dissolved in non-HBA solvents.

Rather than being based on solvent effects on single indicators, as has been the case for most earlier solvent property scales,<sup>1,12</sup> the solvatochromic parameters were

arrived at by averaging multiple normalized solvent effects on a variety of properties involving many diverse types of indicators. After a series of successive approximations, most of the values have "settled down" (i.e., additional results are not likely to materially change the averages), and we are now fairly well satisfied with the  $\pi^*$  and  $\beta$  values of most HBA solvents and the  $\pi^*$  and  $\alpha$  values of most HBD solvents, but the  $\beta$  values of a number of important amphiprotic solvents (most HBD solvents are amphiprotic) are still somewhat uncertain and remain subject to change.

The solvatochromic parameters were intended for use in *linear solvation energy relationships* (LSER's) or, in the case of solute-solute interactions, linear complexation energy relationships of the generalized form of eq 1. The  $XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H + e\xi$  (1)

$\delta$  parameter in eq 1 is a "polarizability correction term" equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents. The  $\delta$  values reflect the fact that, as a general rule, differences in solvent polarizability [expressed in terms of the refractive index function  $(n^2 - 1)/(2n^2 + 1)$ ] are significantly greater between these classes of solvents than within the classes. The coefficient of  $\delta$  (the  $d$  term) is zero for all electronic spectra that are shifted bathochromically (to lower frequencies) with increasing solvent dipolarity (i.e.,  $\nu_{\max}$  is linear with  $\pi^*$  with all non-hydrogen bonding solvents considered together). For spectra that are shifted hypsochromically (to higher frequencies), and for other XYZ's, the  $d$  term is zero only when the individual families of solvents are considered separately; when all solvents need to be considered together, the  $d$  term is finite and (usually) negative. The sign and magnitude of the  $d$  term have been related to the dipolarity/polarizability blend in the solvent effect on XYZ, expressed in terms of functions of the refractive index and either the dipole moment or the dielectric constant.<sup>13</sup>

The  $\delta_H$  term in eq 1 is the *Hildebrand solubility parameter*,<sup>14</sup> a measure of the solvent/solvent interactions that are interrupted in creating a cavity for the solute (the cavity term), and is important when dealing with enthalpies or free energies of solution or of transfer between

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(2) (a) Kamlet, M. J.; Abboud, J.-L. M.; Taft, R. W. *J. Am. Chem. Soc.* 1977, 99, 6027. (b) Chawla, B.; Pollack, S. K.; Lebrilla, C. B.; Kamlet, M. J.; Taft, R. W. *Ibid.* 1981, 103, 6924.

(3) Kamlet, M. J.; Hall, T. N.; Boykin, J.; Taft, R. W. *J. Org. Chem.* 1979, 44, 2599.

(4) Abboud, J.-L. M.; Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* 1977, 99, 8325.

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(9) Kamlet, M. J.; Jones, M. E.; Taft, R. W.; Abboud, J.-L. M. *J. Chem. Soc., Perkin Trans. 2* 1979, 342.

(10) (a) Kamlet, M. J.; Solomonovici, A.; Taft, R. W. *J. Am. Chem. Soc.* 1979, 101, 3734. (b) Taft, R. W.; Gramstad, T.; Kamlet, M. J. *J. Org. Chem.* 1982, 47, 4557.

(11) We have also recently shown that the effects of HBA base solvents or reactants on certain properties of nonprotonic Lewis acid indicators are also linear with  $\beta$ : (a) Taft, R. W.; Pienta, N. J.; Kamlet, M. J.; Arnett, E. M. *J. Org. Chem.* 1981, 46, 661. (b) Taft, R. W.; Kamlet, M. J. *Org. Magn. Reson.* 1980, 14, 485.

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(13) Taft, R. W.; Abboud, J.-L. M.; Kamlet, M. J. *J. Am. Chem. Soc.* 1981, 103, 1080.

(14) Hildebrand, J. H.; Scott, R. L. "The Solubility of Nonelectrolytes", 3rd ed.; Dover Publ.: New York, 1964. Hildebrand, J. H.; Scott, R. L. "Regular Solutions"; Prentice Hall: Englewood Cliffs, NJ, 1962.

solvents, or with gas-liquid chromatographic partition coefficients. The  $\xi$  parameter, a *coordinate covalency* measure, equal to  $-0.20$  for  $\text{P}=\text{O}$  bases,  $0.0$  for  $\text{C}=\text{O}$ ,  $\text{S}=\text{O}$ , and  $\text{N}=\text{O}$  bases,  $0.20$  for single-bonded oxygen bases,  $0.60$  for pyridine bases, and  $1.00$  for  $\text{sp}^3$ -hybridized amine bases, has been useful in correlating certain types of basicity properties.<sup>15</sup> The  $s, d, a, b, h,$  and  $e$  coefficients in eq 1 measure the relative susceptibilities of  $XYZ$  to the indicated solvent property scales. The  $\pi^*$ ,  $\alpha$ ,  $\beta$ , and  $\xi$  parameters are roughly normalized to cover a range from near  $0.0$  to near  $1.0$  so that the  $a/s, b/s, a/b,$  and  $e/\beta$  ratios should provide convenient measures of the relative contributions of the indicated solvent properties.

We next show how, by a judicious choice of solvents and reactants and/or indicators, it has usually been possible to reduce eq 1 to a more manageable form. Thus, for example, we have reported one-, two-, or three-parameter correlations involving logarithms of rate constants, equilibrium constants, fluorescence lifetimes, and GLC partition coefficients, positions and intensities of maximal absorption in NMR, ESR, IR, and UV/vis spectra, NMR coupling constants, free energies and enthalpies of solution and of transfer of dipolar solutes between solvents, and enthalpies and free energies of formation of hydrogen-bonded and Lewis acid/base complexes. Examples of the various types of correlations are as follows.

#### Correlations with $\pi^*$ and with $(\pi^* + d\delta)$

The UV/vis spectrum of *N,N*-diethyl-4-nitroaniline (1), a nonprotonic indicator ( $b = 0$ ) in non-HBA solvents ( $\alpha = 0$ ), is shifted bathochromically with increasing solvent dipolarity ( $d = 0$ ). From the Franck-Condon principle, the ground and electronic excited states occupy the same volume, so that  $h = 0$ . Thus, solvent effects on  $\nu(1)_{\text{max}}$  depend only on  $\pi^*$ , as is shown in eq 2

$$\nu(1)_{\text{max}} = 27.52 - 3.18\pi^* (10^3 \text{ cm}^{-1}) \quad (2)$$

where  $n$  (the number of solvents studied) = 28,  $r$  (the correlation coefficient) = 0.994, and  $sd$  (the standard deviation) =  $0.10 \times 10^3 \text{ cm}^{-1}$ . We have reported similar correlations with  $\pi^*$  for  $47 \text{ p} \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic spectral transitions.<sup>2a</sup>

With other types of  $XYZ$ 's, separate regression lines with  $\pi^*$  are observed for results in the individual solvent families. Thus, for rates of the Menschutkin reaction of tri-*n*-propylamine with methyl iodide<sup>3,16</sup> (the reactants are nonprotic, thus  $b = 0$ ) in non-HBD solvents ( $\alpha = 0$ ), the correlation equations are eq 3a for 15 nonchlorinated al-

$$\log k = -4.38 + 4.96\pi^* \quad (3a)$$

$$r = 0.994 \quad sd = 0.16$$

$$\log k = -4.40 + 4.70\pi^* \quad (3b)$$

$$r = 0.993 \quad sd = 0.13$$

$$\log k = -4.01 + 3.98\pi^* \quad (3c)$$

$$r = 0.988 \quad sd = 0.17$$

iphatic solvents, eq 3b for 11 polychlorinated aliphatics, and eq 3c for 18 aromatic solvents. The  $d$  value is calculated to be  $-0.09$ ,<sup>17</sup> and the correlation with  $(\pi^* - 0.09\delta)$

is given by eq 3d. As with other correlations involving

$$\log k = -4.18 + 4.66(\pi^* - 0.09\delta) \quad (3d)$$

$$n = 44 \quad r = 0.990 \quad sd = 0.17$$

reaction rate and equilibrium constants, there might be a difference between reactant and product or transition-state volumes. This might lead to a dependence also on  $\delta_{\text{H}}$ . If there is such a dependence in the present instance, it is statistically insignificant and is not included in eq 3a-d.

As another example, Dimroth and Reichardt's  $E_T(30)$  "solvent polarity" scale is based on the "solvatochromiebande" of 4-(2,4,6-triphenylpyridino)-2,6-diphenylphenoxide betaine (2), a nonprotonic indicator ( $b = 0$ ), whose spectrum is shifted hypsochromically with increasing solvent dipolarity ( $d \neq 0$ ).<sup>2a,12</sup> In nonprotonic solvents ( $\alpha = 0$ ), the correlation equations are eq 4a for

$$\nu(2)_{\text{max}} = 10.80 + 4.84\pi^* (10^3 \text{ cm}^{-1}) \quad (4a)$$

$$r = 0.974 \quad sd = 0.39 \times 10^3 \text{ cm}^{-1}$$

$$\nu(2)_{\text{max}} = 9.56 + 5.93\pi^* (10^3 \text{ cm}^{-1}) \quad (4b)$$

$$r = 0.985 \quad sd = 0.26 \times 10^3 \text{ cm}^{-1}$$

$$\nu(2)_{\text{max}} = 8.88 + 5.82\pi^* (10^3 \text{ cm}^{-1}) \quad (4c)$$

$$r = 0.967 \quad sd = 0.32 \times 10^3 \text{ cm}^{-1}$$

16 nonchlorinated aliphatic solvents, eq 4b for 7 polychlorinated aliphatics, and eq 4c for 9 aromatic solvents. The  $d$  term is calculated to be  $-0.23$ ,<sup>17</sup> and the correlation with  $(\pi^* - 0.23\delta)$  is given by eq 4d for the 32 nonprotonic solvents.

$$\nu(2)_{\text{max}} = 10.60 + 5.12(\pi^* - 0.23\delta) \quad (4d)$$

$$r = 0.972 \quad sd = 0.33 \times 10^3 \text{ cm}^{-1}$$

#### Correlations Also Involving $\alpha$ and/or $\beta$

Continuing the discussion of the  $E_T(30)$  scale, in HBD solvents ( $\alpha \neq 0$ ), the spectrum of the betaine is shifted further hypsochromically (relative to predictions by eq 4d) due to type-A hydrogen bonding<sup>18</sup> to the phenoxide oxygen. The magnitudes of the enhanced shifts, represented by  $\Delta\Delta\nu(2-\pi^*)$ , and calculated by eq 5, are linear with and

$$\Delta\Delta\nu(2-\pi^*) = \nu(2)_{\text{max}}^{\text{obsd}} - \nu(2)_{\text{eq 4}}^{\text{calcd}} \quad (5)$$

very nearly proportional to the solvent  $\alpha$  values. The regression equation of  $\Delta\Delta\nu(2-\pi^*)$  with  $\alpha$ , force fitted through the origin to reflect the necessary direct proportionality, is given by eq 6. Combining eq 4d and 6, the

$$\Delta\Delta\nu(2-\pi^*) = 5.78\alpha \pm 0.22 (10^3 \text{ cm}^{-1}) \quad (6)$$

$$n = 12 \quad r = 0.986$$

total solvatochromic equation for  $\nu(2)_{\text{max}}$  in 44 protonic and nonprotonic solvents of all types is given by eq 7. Thus,

$$\nu(2)_{\text{max}} = 10.60 + 5.12(\pi^* - 0.23\delta) + 5.78\alpha (10^3 \text{ cm}^{-1}) \quad (7)$$

a series of sequential correlations, wherein we consider different solvent subsets at the various stages (and which we refer to as the *stepwise version of the solvatochromic*

(15) Taft, R. W.; Gal, J. F.; Maria, P. C.; Kamlet, M. J., to be submitted for publication in *J. Am. Chem. Soc.* (deals with the  $\xi$  parameter).

(16) Lassau, C.; Jungers, J. C. *Bull. Soc. Chim. Fr.* 1968, 2678.

(17) The  $d$  term is estimated through the equation  $d = 2\Delta XYZ/[s(\text{al}) + s(\text{ar})]$ , where  $\Delta XYZ$  is the difference between the values calculated through the aliphatic and aromatic regression equations at  $\pi^* = 0.7$  and  $s(\text{al})$  and  $s(\text{ar})$  are the slopes of those regression equations.

(18) In type-A hydrogen bonding, the solute acts as HBA base and the solvent as HBD acid; in type-B hydrogen bonding, the roles are reversed. In type-AB hydrogen bonding, which we will document in detail in a future paper, the solute acts simultaneously as HBD acid and HBA base at the same site, associating (usually) with at least two molecules of amphiprotic solvent in a probably cyclic complex. We have so far observed type-AB hydrogen bonding with  $\text{sp}^3$ - but not  $\text{sp}^2$ -hybridized amine indicators.

comparison method), allows us to unravel and quantify the multiple effects of solvent dipolarity, polarizability and hydrogen bonding on the UV/vis spectrum of 2.

An alternative version of the solvatochromic comparison method involves multiple linear regression analysis (multiple-parameter least-squares correlation). We take as an example Gutmann's solvent "acceptor number" (AN) scale, based on  $^{31}\text{P}$  NMR solvent shifts of triethylphosphine oxide (a nonprotonic indicator,  $b = 0$ ) and purported to be a measure of solvent electrophilicity.<sup>11a,19</sup> If we consider protonic and nonprotonic aliphatic solvents ( $\delta = 0$ ,  $\alpha \neq 0$ ), the stepwise method (first AN vs.  $\pi^*$ , then  $\Delta\Delta\text{AN}$  vs.  $\alpha$ ) leads to eq 8a, and multiple-parameter

$$\text{AN} = 0.40 + 16.4\pi^* + 31.1\alpha \quad (8a)$$

$$n = 17 \quad r = 0.994 \quad \text{sd} = 1.6$$

$$\text{AN} = 0.04 + 16.2\pi^* + 33.0\alpha \quad (8b)$$

$$r = 0.996 \quad \text{sd} = 1.5$$

least-squares correlation of AN with  $\pi^*$  and  $\alpha$  leads to eq 8b. Considering that seven  $\pi^*$  values of protic solvents that served as input to eq 8b did not contribute to the determination of  $s$  in eq 8a, the agreement between the two methods is quite satisfactory. If aromatic solvents are included in the correlation, the  $d$  value is calculated to be  $-0.08$ ,<sup>17</sup> and the multiple-parameter least-squares correlation of AN with  $(\pi^* - 0.8\delta)$  and  $\alpha$  leads to eq 9.

$$\text{AN} = 1.04 + 15.4(\pi^* - 0.08\delta) + 32.6\alpha \quad (9)$$

$$n = 22 \quad r = 0.994 \quad \text{sd} = 0.17$$

Equations 7 and 9 show that when multiple interacting effects are correctly unravelled, Dimroth and Reichardt's  $E_T(30)$ , purported to be a scale of solvent polarity, and Gutmann's AN, purported to be a scale of solvent electrophilicity, both measure different linear combinations of the two properties.

An example of a correlation with  $\pi^*$  and  $\beta$  involves the UV/vis spectrum of 3,5-dinitroaniline (3),<sup>9</sup> a protonic indicator whose absorption maximum is shifted bathochromically with increasing solvent dipolarity and with type-B hydrogen bonding by the amine protons to HBA solvents ( $d = 0$ ,  $b \neq 0$ ). The stepwise and multiple linear regression equations for  $\nu(3)_{\text{max}}$  in 33 non-HBD solvents ( $\alpha = 0$ ) are given by eq 10a and 10b. Again the agreement

$$\nu(3)_{\text{max}} = 27.60 - 1.42\pi^* - 2.80\beta \quad (10^a)$$

$$r = 0.995 \quad \text{sd} = 0.10 \times 10^3 \text{ cm}^{-1}$$

$$\nu(3)_{\text{max}} = 27.57 - 1.36\pi^* - 2.82\beta \quad (10^b)$$

$$r = 0.995 \quad \text{sd} = 0.10 \times 10^3 \text{ cm}^{-1}$$

between the two versions of the solvatochromic comparison method is highly satisfactory.

This is quite important, because in other studies we have sometimes had insufficient data in non-hydrogen-bonding solvents to determine solvatochromic equations by the stepwise method, so that it was necessary to use the method of multiple linear regression analysis. In several such instances we were faced with referees' assertions that, with the greater number of adjustable parameters, the effects of the individual solvent properties were less precisely defined (and, indeed, such a reaction should be natural from anyone on seeing eq 1 for the first time). We therefore emphasize the excellent correspondence between the two methods (see Table II of ref 9 for further examples)

since we believe that it is difficult to find imprecision in the stepwise method, which involves successive single-parameter correlations and wherein the statistical goodness of fit is confirmed at every stage of the calculation.

Where we use the multiple linear regression method, it is, of course, correct to say that with the inclusion of each new adjustable parameter (exploratory variable), the goodness of fit, as judged by the multiple-correlation constant, must either improve or remain the same. There are statistical procedures based either on the  $t$  test or  $F$  statistic to demonstrate whether or not the inclusion of the new exploratory variable is statistically justified, and, where appropriate, we have applied such statistical tests.

Examples of other types of properties that we have correlated with  $\pi^*$  or  $(\pi^* + d\delta)$  and  $\beta$  are given by  $^{13}\text{C}$  NMR shifts and  $J(^{13}\text{C}, ^1\text{H})$  coupling constants of chloroform, using data reported by Lichter and Roberts.<sup>11b,20,21</sup>

$$^{13}\text{C NMR } \Delta\delta = -0.27 + 1.09\pi^* + 3.10\beta \text{ ppm} \quad (11a)$$

$$n = 10 \quad r = 0.985^{20}$$

$$J(^{13}\text{C}, ^1\text{H}) = 205.3 + 4.85(\pi^* - 0.40\delta) + 7.63\beta \text{ Hz} \quad (11b)$$

$$n = 9 \quad r = 0.996$$

In situations where both solvents and solutes have been hydrogen-bond donors (and hence usually amphiprotic), it has proven quite difficult to untangle solvent dipolarity/polarizability, type-B hydrogen bonding, and variable self-association effects<sup>5,6</sup> from (usually multiple) type-A hydrogen-bonding interactions. Also, there are often further complications from type-AB hydrogen-bonding interactions<sup>18</sup> (whose effects we can identify but have not yet been able to quantify). For these reasons we have demonstrated solvatochromic equations with unambiguously distinct dependences on the three solvatochromic parameters,  $\pi^*$ ,  $\alpha$ , and  $\beta$  in only a few instances.

One such instance involves  $\nu_{\text{max}}$  in the fluorescence spectrum ( $d \neq 0$ ) of 4-amino-7-methylcoumarin (4), an HBD indicator ( $b \neq 0$ ) in 11 aliphatic HBD and non-HBD solvents ( $\delta = 0$ ,  $\alpha \neq 0$ ).<sup>22,23</sup> The amine protons of 4 form type-B hydrogen bonds to HBA and amphiprotic solvents, and HBD solvents form type-A hydrogen bonds to the C=O oxygen of 4. The effects of both types of hydrogen bonding and of increasing solvent dipolarity/polarizability are to shift  $\nu(4)_{\text{max}}^{\text{fluo}}$  bathochromically, the solvatochromic equation being given by eq 12.

$$\nu(4)_{\text{max}}^{\text{fluo}} = 26.71 - 2.02\pi^* - 1.58\alpha - 1.32\beta \quad (12)$$

$$r = 0.997$$

### Correlations with the Hildebrand Solubility Parameter $\delta_H$

The  $\delta_H$  parameter (usually represented as  $\delta$ ; the subscript is to distinguish from the polarizability correction term), variously described as the square root of the internal pressure or of the cohesive energy density, is defined by eq 13 where  $-E$  is the molal heat of vaporization to a gas

$$\delta_H = (-E/V)^{1/2} \quad (13)$$

at zero pressure and  $V$  is the molal volume.<sup>24</sup> A com-

(20) A small  $d$  term (of about  $-0.02$ ) has been ignored in this correlation.

(21) Lichter, R. L.; Roberts, J. D. *J. Phys. Chem.* 1970, 74, 912.

(22) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *Chem. Phys. Lett.* 1981, 77, 69.

(23) Coosemans, L.; de Schryver, F. C.; van Dormael, A. *Chem. Phys. Lett.* 1979, 65, 95.

(19) Gutmann, V. *CHEMTECH* 1977, 255. Gutmann, V. "The Donor-Acceptor Approach to Molecular Interactions"; Plenum Press: New York, 1972; Chapter 2.

prehensive collection of  $\delta_H$  values has been reported by Barton.<sup>25</sup> From eq 13 it is seen that  $\delta_H$  is a measure of the energy required to separate solvent molecules from one another and, consistent with this definition,  $\delta_H$  appears to be a good measure of the solvent/solvent interactions that are interrupted in creating a suitably sized cavity for the solute in the solvent.

Free energies of solution of dipolar and nondipolar nonprotonic solutes ( $b = 0$ ) in nonprotonic aliphatic select solvents ( $d = 0, \alpha = 0$ ) are well correlated by equations of the form of eq 14, with the sign of  $h$  positive (the endogenic

$$\Delta G_s^\circ = (\Delta G_s^\circ)_0 + s\pi^* + h\delta_H \quad (14)$$

cavity term) and the sign of  $s$  negative (the exogenic solute/solvent interaction term).

For nondipolar solutes, the solute/solvent interaction term is negligible ( $s = 0$ ), and good linear regression is observed with  $\delta_H$ . An example is given by eq 15 for *n*-octane solute:

$$\Delta G_s^\circ(n\text{-C}_8\text{H}_{18}) = -6.63 + 0.56\delta_H \text{ kcal/mol} \quad (15)$$

$$n = 15 \quad r = 0.974 \quad \text{sd} = 0.26 \text{ kcal/mol}$$

We have reported similar correlations, with quite satisfactory precision, for free energies of solution of the rare gases from helium to xenon, the straight chain hydrocarbons from  $C_1$  to  $C_8$ , cyclohexane, and tetramethyltin. Both the slopes,  $h$ , and the intercepts  $(\Delta G_s^\circ)_0$ , were shown to be nicely linear with solute molecular volumes.<sup>26</sup>

In the case of dipolar solutes, statistically significant dependences on both  $\delta_H$  and  $\pi^*$  are observed, with the positive (endogenic)  $h$  term becoming larger the greater the solute molecular volume and the negative (exogenic)  $s$  term becoming larger the greater the solute dipole moment or charge separation. Representative examples are given by eq 16–19.<sup>27</sup> Although eq 19 involves a free energy

$$\Delta G_s^\circ(t\text{-BuCl}) = -2.14 + 0.26\delta_H - 0.56\pi^* \text{ kcal/mol} \quad (16)$$

$$n = 9 \quad r = 0.959$$

$$\Delta G_s^\circ(2\text{-butanone}) = -1.78 + 0.17\delta_H - 1.51\pi^* \text{ kcal/mol} \quad (17)$$

$$n = 17 \quad r = 0.924$$

$$\Delta G_s^\circ(\text{nitromethane}) = -1.54 + 0.21\delta_H - 3.44\pi^* \text{ kcal/mol} \quad (18)$$

$$n = 18 \quad r = 0.991$$

$$\Delta G_t^\circ(\text{Et}_4\text{N}^+\text{I}^-) = 9.26 + 0.36\delta_H - 14.62\pi^* \text{ kcal/mol} \quad (19)$$

$$n = 13 \quad r = 0.990$$

of transfer between solvents rather than a free energy of solution, the  $s$  and  $h$  terms have the same meanings and can validly be compared with the corresponding quantities in eq 16–18.

Solvent dipolarity and polarizability are important contributors to both  $\pi^*$  and  $\delta_H$  (with lone-electron-pair repulsions probably having more important influences on  $\delta_H$ ); also, the correlation coefficient,  $r$ , for the linear re-

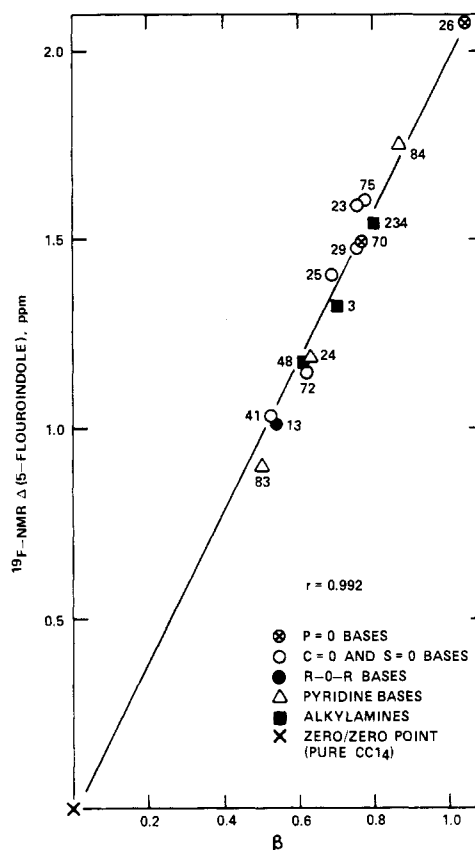


Figure 1.  $^{19}\text{F}$ -NMR  $\Delta$  of 5-fluoroindole plotted against  $\beta$ .

gression of  $\pi^*$  with  $\delta_H$  is 0.886.<sup>26</sup> It seems remarkable, therefore, that in most cases the dependences on the two parameters can be unraveled by multiple linear regression analysis to give the correct signs, and reasonable progressions in the magnitudes of the  $s$  and  $h$  coefficients in eq 14 (such unscrambling can be accomplished only when the data set includes solvents that are out-of-line in the  $\pi^*$  vs.  $\delta_H$  correlation).<sup>28</sup>

All the above cases of dependences on  $\delta_H$  have involved the free energy of solution or of transfer of a single species. However, if correlations are carried out involving rate or equilibrium constants, the  $h\delta_H$  quantity will then represent the solvent effect on the differential cavity term, i.e.,  $G_{\text{cav}}(\text{products}) - G_{\text{cav}}(\text{reactants})$ . Since the sizes or volumes of species involved in equilibria or rates of reactions will not change drastically in the course of the process, the differential cavity term will usually be very small, and it is expected that there will be little or no observed dependence on  $\delta_H$  in these latter cases.

### Correlations with $\beta$ and the Coordinate Covalency Parameter $\xi$

In earlier papers we have described two general types of correlations with the basicity parameter  $\beta$ : (1) correlations where, after accounting for dipolarity/polarizability effects or dipole/dipole interaction effects, if necessary, the property studied is linear with  $\beta$  with all bases considered together and (2) correlations where good linearity between the property and  $\beta$  is observed only when families of bases having similar types of hydrogen-bond acceptor sites are considered separately. In the latter instances, regression lines with  $\beta$  are usually nearly parallel. We refer to relationships of the first types as "family independent"

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(28) Solvents that are out-of-line in the  $\pi^*$  vs.  $\delta_H$  correlation include hexane, cyclohexane, triethylamine, diethyl ether, and di-*n*-butyl ether.

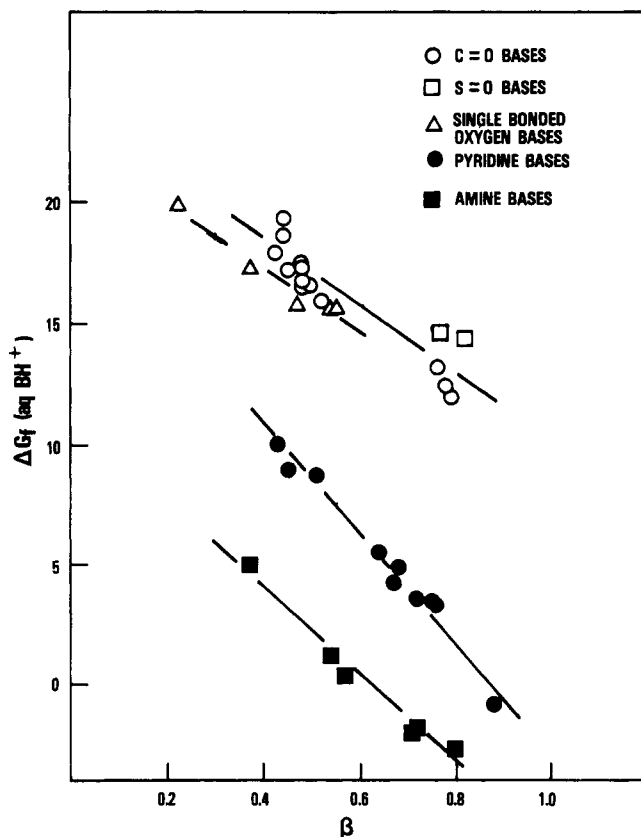


Figure 2.  $\Delta G_f(\text{aq BH}^+)$  plotted against  $\beta$  of B.

(FI) correlations and to those of the second type as "family dependent" (FD).

As a general rule, FI relationships have been observed with electronic spectral hydrogen-bonding shifts, NMR spectral shifts and coupling constants, and free energy properties (e.g., logarithms of formation constants) of hydrogen-bonded complexes. A good example is provided by  $^{19}\text{F}$  NMR shifts of 5-fluoroindole complexes with HBA bases in  $\text{CCl}_4$ .<sup>11b,29</sup> The linear regression equation involving many types of bases is given by eq 20. A plot of the data is shown in Figure 1.

$$^{19}\text{F NMR } \Delta\delta = -0.066 + 2.06\beta \text{ ppm} \quad (20)$$

$$n = 15 \quad r = 0.982 \quad \text{sd} = 0.06 \text{ ppm}$$

FD correlations have included infrared stretching frequency shifts,  $\Delta\nu(\text{X-H, free minus hydrogen bonded})$ , enthalpies of formation of base complexes with hydrogen-bond donor acids and Lewis acids, free energies of formation of base complexes with Lewis acids, and, most particularly, the property of most widespread interest in any discussion of acidity/basicity, aqueous  $\text{p}K_a$ . We have recently shown<sup>15</sup> that the extent of family dependence could be quantified by, and the FD properties correlated through, the use of an empirical coordinate covalency parameter,  $\xi$ , and equations of the form of eq 21. As has

$$XYZ = XYZ_0 + b\beta + e\xi \quad (21)$$

been mentioned, values of  $\xi$  assigned to the various families are  $-0.20$  for  $\text{P}=\text{O}$  bases,  $0.00$  for  $\text{C}=\text{O}$ ,  $\text{S}=\text{O}$ , and  $\text{N}=\text{O}$  bases,  $0.20$  for single-bonded oxygen bases,  $0.60$  for pyridine bases, and  $1.00$  for  $\text{sp}^3$ -hybridized amine bases.

(29) We are not considering the property of the HBA base acting as solvent but rather as solute in a non-HBA solvent. It is significant that for non-self-associating HBA bases,  $\beta_i$  values have been similar, irrespective of whether the HBA base was a solvent or a solute in relatively dilute solution.

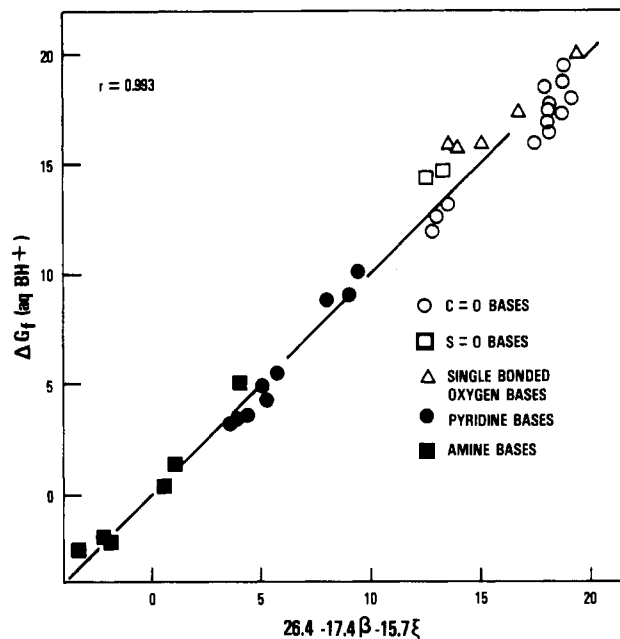


Figure 3.  $\Delta G_f(\text{aq BH}^+)$  as a combined function of  $\beta$  and  $\xi$ .

The most important example of a correlation by eq 21 has involved free energies of proton transfer to the aqueous bases from aqueous  $\text{NH}_4^+$ ,  $\Delta G_f(\text{aq BH}^+)$ , which are linear

$$\Delta G_f(\text{aq BH}^+) = 26.4 - 17.4\beta - 15.7\xi \text{ kcal/mol} \quad (22)$$

$$n = 35 \quad r = 0.992$$

with the base  $\text{p}K_a$  values.<sup>15</sup> Plots of  $\Delta G_f(\text{aq BH}^+)$  against  $\beta$  and against  $\Delta G_{\text{eq } 22}^{\text{calcd}}$  are shown in Figures 2 and 3. We believe this correlation to be the first instance wherein measures of hydrogen-bonding basicity and proton-transfer basicity involving all of the above families of bases have been quantitatively related to one another within the framework of the same calculational method.

Another example of a correlation of a frequently reported type of FD property with  $\beta$  and  $\xi$  is given by  $\Delta\nu(\text{O-H, free minus hydrogen bonded})$  of phenol complexes with the HBA bases in  $\text{CCl}_4$ .<sup>15,30</sup>

$$\Delta\nu(\text{O-H}) = -34.5 + 512\beta + 313\xi \text{ cm}^{-1} \quad (23)$$

$$n = 43 \quad r = 0.989$$

We have pointed out that there are some formal and conceptual similarities and some important differences between eq 21 and the Drago E-C treatment.<sup>15,31</sup> We have also set forth some important caveats regarding correlations by eq 21. For example, steric effects in acid/base complexing can lead to severe deviations from eq 21. Aqueous ionic solvation energies of  $\text{BH}^+$  are large and variable,<sup>32</sup> but the relationship between the hydration energies and the corresponding gas-phase basicities frequently involves reciprocal family behavior,<sup>33</sup> explaining in part the tendency of  $\Delta G_f(\text{aq BH}^+)$  to follow eq 22.<sup>34</sup> The formation of many acid/base complexes is accompanied by significant

(30) Data in ref 10a.

(31) For a summary, see: Drago, R. S. *Struct. Bond. (Berlin)* 1973, 15, 72; *Coord. Chem. Rev.* 1980, 33, 251.

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Table I. Comprehensive Table of Solvatochromic Parameters<sup>a</sup>

no. <sup>b</sup>	solvents (and some solid bases)	$\pi^*$	$\beta$	$\alpha$
Aliphatic Hydrocarbons				
1	<i>n</i> -hexane, <i>n</i> -heptane	-0.08	0.00	0.00
2	cyclohexane	0.00	0.00	0.00
Ethers and Orthoesters ( $\xi = 0.20$ )				
4	diisopropyl ether	0.27	0.49	0.00
5	di- <i>n</i> -butyl ether	0.24	0.46	0.00
7	diethyl ether	0.27	0.47	0.00
9	dioxane	0.55	0.37	0.00
13	tetrahydrofuran	0.58	0.55	0.00
17	anisole	0.73	0.22	0.00
40	tetrahydropyran	0.51	0.54	0.00
46	dibenzyl ether	0.80	0.41	0.00
59	diphenyl ether	0.66	0.13	0.00
61	1,2-dimethoxyethane	0.53	0.41	0.00
86	di- <i>n</i> -propyl ether	((0.27))	0.46	0.00
87	phenetole	((0.69))	0.20	0.00
88	bis(2-methoxyethyl) ether	0.64		0.00
133	trimethyl orthoacetate	0.35		0.00
134	trimethyl orthoformate	0.58		0.00
Aldehydes and Ketones ( $\xi = 0.00$ )				
16	2-butanone	0.67	0.48	0.06
18	acetone	0.71	0.48	0.08
36	1,1,1-trichloroacetone		0.14	
41	cyclohexanone	0.76	0.53	
51	cyclopentanone	0.76	0.52	
58	acetophenone	0.90	0.49	
65	methyl <i>tert</i> -butyl ketone		0.48	
66	benzaldehyde	((0.92))	0.44	0.00
71	dimethyl- $\gamma$ -pyrone		0.79	
76	benzophenone		0.44	0.00
77	biacetyl		0.31	
98	3-heptanone	0.59		
131	phenylacetone	0.88		
139	<i>sym</i> -dichloroacetone		0.34	
140	methyl isopropyl ketone		0.48	
141	<i>p</i> -methoxyacetophenone		0.54	
142	acetylferrocene		0.58	
143	flavone		0.66	
144	<i>p</i> -nitrobenzaldehyde		0.32	0.00
145	propionaldehyde		0.40	
146	butyraldehyde		0.41	
147	<i>p</i> -chlorobenzaldehyde		0.42	0.00
148	<i>p</i> -methoxybenzaldehyde		0.49	0.00
149	<i>p</i> -(dimethylamino)benzaldehyde		0.59	0.00
150	2-naphthaldehyde		0.43	0.00
151	di- <i>tert</i> -butyl ketone		0.48	0.00
152	cinnamaldehyde		0.53	0.00
153	propiophenone		0.43	
154	3-pentanone	((0.72))	0.45	
155	2-pentanone		0.50	
156	isobutyrophenone		0.42	
157	<i>p</i> -chloroacetophenone		0.46	
158	<i>p</i> -methylacetophenone		0.51	
248	dicyclopropyl ketone	0.63	0.53	
249	methyl cyclopropyl ketone	0.66	0.52	
Esters ( $\xi = 0.00$ )				
11	ethyl acetate	0.55	0.45	0.00
27	butyrolactone	0.87	0.49	0.00
38	butyl acetate	0.46		0.00
39	ethyl chloroacetate	0.70	0.35	0.00
47	ethyl benzoate	0.74	0.41	0.00
52	methyl acetate	0.60	0.42	0.00
55	methyl formate	0.62	0.37	0.00
64	ethyl propionate	((0.47))	0.42	0.00
85	diethyl carbonate	0.45	0.40	0.00
86	diethyl malonate	0.64		
95	ethyl acetoacetate	0.61		
96	ethyl trichloroacetate	0.61	0.25	0.00
136	methyl trifluoroacetate	0.39		0.00
137	propylene carbonate	((0.83))	0.40	0.00
138	ethyl formate	0.61	0.36	0.00
171	phenyl benzoate		0.39	0.00
172	ethyl <i>p</i> -nitrobenzoate		0.40	0.00
173	dimethyl carbonate		0.38	0.00

Table I (Continued)

no. <sup>b</sup>	solvents (and some solid bases)	$\pi^*$	$\beta$	$\alpha$
174	methyl benzoate		0.39	0.00
175	ethyl trifluoroacetate		0.19	0.00
Amides, Carbamates, and Ureas ( $\xi = 0.00$ )				
23	dimethylacetamide	0.88	0.76	0.00
25	dimethylformamide	0.88	0.69	0.00
28	<i>N</i> -methylpyrrolidone	0.92	0.77	0.00
69	<i>N,N</i> -dimethyl trifluoroacetamide		0.46	0.00
72	<i>N,N</i> -dimethyl chloroacetamide		0.62	0.00
75	tetramethylurea	0.83	0.80	0.00
159	<i>N,N</i> -dimethyl- <i>p</i> -nitrobenzamide		0.61	0.00
160	<i>N,N</i> -dimethylbenzamide		0.72	0.00
161	<i>N,N</i> -di- <i>n</i> -hexylacetamide		0.77	0.00
162	<i>N,N</i> -diethylacetamide		0.78	0.00
163	<i>N,N</i> -diethylbenzamide		0.70	0.00
164	<i>N</i> -acetylpiperidine		0.73	0.00
165	<i>N,N</i> -diphenylacetamide		0.64	0.00
166	tetraethylurea		0.71	0.00
167	<i>N</i> -methylpyridone		0.78	0.00
167	ethyl diethylcarbamate		0.65	0.00
169	<i>N,N</i> -diethylpropionamide		0.75	0.00
170	<i>N,N</i> -diphenylpropionamide		0.61	0.00
204	formamide	0.97		0.71
Acids, Acid Halides, Acid Anhydrides ( $\xi = 0.00$ )				
34	acetic anhydride	0.76		0.00
176	benzoyl fluoride		0.16	0.00
177	propionyl fluoride		0.20	0.00
178	benzoyl chloride		0.20	0.00
179	benzoyl bromide		0.16	0.00
201	acetic acid	0.64		1.12
203	trifluoroacetic acid	0.50		
Amines ( $\xi = 1.00$ )				
3	triethylamine	0.14	0.71	0.00
48	tri- <i>n</i> -butylamine	0.16	0.62	0.00
49	<i>N,N</i> -dimethylbenzylamine	0.49	0.57	0.00
57	<i>N,N</i> -dimethylaniline	0.90		0.00
225	triallylamine		0.54	0.00
226	tri- <i>n</i> -propylamine		0.56	0.00
227	<i>N,N</i> -dimethyl- <i>N</i> -propylamine		0.68	0.00
228	<i>N,N</i> -dimethyl- <i>N</i> -cyclohexylamine		0.71	0.00
229	$\beta,\beta,\beta$ -trifluoroethylamine		0.37	
230	propargylamine		0.57	
231	cyclopropylamine		0.60	
232	benzylamine		0.63	
233	<i>n</i> -butylamine		0.72	
234	quinuclidine		0.80	0.00
235	<i>N</i> -methylimidazole		0.82	0.00
236	1,4-diazabicyclo[2.2.2]octane (Dabco)		0.73	0.00
237	di- <i>n</i> -butylamine		0.70	
Sulfoxides ( $\xi = 0.00$ )				
29	dimethyl sulfoxide	1.00	0.76	0.00
45	ethyl sulfate	0.69		0.00
56	sulfolane	0.98		0.00
67	diphenyl sulfoxide		0.70	0.00
74	di- <i>n</i> -butyl sulfoxide		0.83	0.00
192	dibenzyl sulfoxide		0.74	0.00
193	methyl phenyl sulfoxide		0.71	0.00
194	methyl <i>p</i> -nitrophenyl sulfoxide		0.60	0.00
195	diethyl sulfite		0.45	0.00
196	di- <i>n</i> -propyl sulfite		0.45	0.00
197	di- <i>n</i> -butyl sulfite		0.46	0.00
198	di- <i>p</i> -tolyl sulfoxide		0.72	0.00
199	diisopropyl sulfoxide		0.78	0.00
200	tetramethylene sulfoxide		0.80	0.00
Phosphine Oxides ( $\xi = -0.20$ )				
19	triethyl phosphate	0.72	0.77	0.00
26	hexamethylphosphoramide	0.87	1.05	0.00
42	tri- <i>n</i> -butyl phosphate	0.65		0.00
68	triphenylphosphine oxide		0.94	0.00
70	trimethyl phosphate			0.00
73	trimethylphosphine oxide		1.02	0.00
180	triphenyl phosphinate		0.62	0.00
181	diethoxy(trichloromethyl)phosphine oxide		0.68	0.00

Table I (Continued)

no. <sup>b</sup>	solvents (and some solid bases)	$\pi^*$	$\beta$	$\alpha$
182	diethoxy(dichloromethyl)phosphine oxide		0.74	0.00
183	diethoxy(chloromethyl)phosphine oxide		0.79	0.00
184	dimethoxyphosphine oxide		0.74	0.00
185	diethoxyphosphine oxide		0.76	0.00
186	diisopropoxyphosphine oxide		0.80	0.00
187	dimethoxyethylphosphine oxide		0.81	0.00
188	diethoxymethylphosphine oxide		0.84	0.00
189	diethoxy(dimethylamino)phosphine oxide		0.88	0.00
190	tri- <i>n</i> -propylphosphine oxide		1.04	0.00
191	triethylphosphine oxide		1.05	0.00
Nitro Compounds and Nitriles ( $\xi$ not yet known)				
31	nitrobenzene	1.01	0.39	0.00
32	nitromethane	0.85		0.22
37	benzonitrile	0.90	0.41	0.00
50	acetonitrile	0.75	0.31	0.19
63	phenylacetone nitrile	0.99		
89	butyronitrile	0.71		
222	<i>p</i> -methoxybenzonitrile		0.46	0.00
223	$\beta$ -ethoxypropionitrile		0.48	0.00
224	<i>p</i> -(dimethylamino)benzonitrile		0.53	0.00
250	propionitrile	0.71	0.37	
Pyridines ( $\xi = 0.60$ )				
24	pyridine	0.87	0.64	0.00
78	4-methylpyridine	((0.84))	0.67	0.00
79	2,6-dimethylpyridine	((0.80))	0.76	0.00
80	2,4,6-trimethylpyridine		0.78	0.00
81	quinoline	((0.92))	0.64	0.00
82	3,5-dichloropyridine		0.42	0.00
83	3-bromopyridine		0.51	0.00
84	4-(dimethylamino)pyridine		0.87	0.00
238	2- <i>n</i> -butylpyridine		0.66	0.00
239	pyrimidine		0.48	0.00
240	2,4-dimethylpyridine		0.74	0.00
241	3-methylpyridine		0.68	0.00
242	4-methoxypyridine		0.72	0.00
Aromatics and Haloaromatics				
8	toluene	0.54	0.11	0.00
14	benzene	0.59	0.10	0.00
15	chlorobenzene	0.71	0.07	0.00
33	bromobenzene	0.79	0.06	0.00
35	<i>p</i> -xylene	0.43		0.00
53	mesitylene	0.41		0.00
60	<i>o</i> -dichlorobenzene	0.80		0.00
62	iodobenzene	0.81		0.00
90	cumene	0.41		0.00
92	<i>m</i> -dichlorobenzene	0.67		0.00
97	fluorobenzene	0.62		0.00
135	<i>m</i> -xylene	0.47		0.00
Haloaliphatics				
6	carbon tetrachloride	0.28	0.00	0.00
10	trichloroethylene	0.53	0.00	0.00
12	1,1,1-trichloroethane	0.49	0.00	0.00
20	1,2-dichloroethane	0.81	0.00	0.00
21	methylene chloride	0.82	0.00	(0.30)
30	chloroform	0.58	0.00	(0.44)
43	tetrachloroethylene	0.28	0.00	0.00
44	1,1,2,2-tetrachloroethane	0.95	0.00	
54	<i>n</i> -butyl chloride	(0.39)	0.00	0.00
91	1,2-dibromoethane	0.75	0.00	0.00
93	<i>trans</i> -1,2-dichloroethylene	0.44	0.00	0.00
132	pentachloroethane	(0.62)	0.00	
251	methylene bromide	(0.92) <sup>c</sup>	0.00	
252	methylene iodide	(1.12) <sup>c</sup>	0.00	
Perfluorinated Compounds				
243	perfluoro- <i>n</i> -octane	-0.41 <sup>d</sup>	0.00	0.00
244	perfluoro- <i>n</i> -heptane	-0.39 <sup>d</sup>	0.00	0.00
245	perfluorodimethyldecalin	-0.33 <sup>d</sup>	0.00	0.00
246	perfluoro tri- <i>n</i> -butylamine	-0.36 <sup>d</sup>		0.00
247	perfluoro- <i>n</i> -hexane	-0.40 <sup>c</sup>	0.00	0.00
Alcohols and Water ( $\xi = 0.20$ )				
101	<i>tert</i> -butanol	0.41	(1.01)	0.68
102	2-propanol	0.48	(0.95)	0.76



Table I (Continued)

no. <sup>b</sup>	solvents (and some solid bases)	$\pi^*$	$\beta$	$\alpha$
103	<i>n</i> -butanol	0.47	(0.88)	0.79
104	ethanol	0.54	(0.77)	0.83
105	methanol	0.60	(0.62)	0.93
106	2-phenylethanol	(0.88)	(0.61)	
107	ethylene glycol	0.92	(0.52)	0.90
109	benzyl alcohol	0.98	(0.50)	
110	2-chloroethanol		(0.31)	
111	water	1.09	(0.18)	1.17
112	<i>n</i> -propanol	0.52		0.78
113	trifluoroethanol	0.73	0.00	1.51
114	hexafluoroisopropanol	0.65	0.00	1.96
115	2-fluoroethanol	(0.72)		
116	2-methoxyethanol	(0.71)		
Amine <i>N</i> -Oxide ( $\xi = 0.00$ )				
221	pyridine <i>N</i> -oxide		0.85	0.00

<sup>a</sup> Data in parentheses are relatively less certain. Data in double parentheses are estimated from eq 24 and 25. <sup>b</sup> Solvent numbering is the same in all papers of the Linear Solvation Energy Relationships and Solvatochromic Comparison Method Series. <sup>c</sup> Bekarek, V.; Jurina, S. *Collect. Czech. Chem. Commun.* 1982, 47, 1060. <sup>d</sup> Brady, J. E.; Carr, P. W. *Anal. Chem.* 1982, 54, 1751.

entropy effects.<sup>35</sup> However, these entropy effects tend to fall into family relationships that follow  $\xi$  values. This accounts, in part, for the tendency of both  $\Delta H_f$  and  $\Delta G_f$  to follow eq 21. Finally, stabilization of bases and their conjugate acids by conjugative  $\pi$ -electron donation may vary nonlinearly with the difference in electron demand between B and BH<sup>+</sup> or between HBA and HBA:HBD. For these and additional reasons to be discussed in a future paper, eq 21 is not expected generally to be a highly precise relationship (although the correlation coefficients for the properties so far studied have been quite respectable).<sup>15</sup> However, with the proper accounting of factors leading to deviations or nonparallel FD behavior, we believe that eq 21 provides a useful quantitative norm for behavior of oxygen and nitrogen bases in properties of many differing types.

### A Comprehensive Collection of the Solvatochromic Parameters

All  $\pi^*$ ,  $\alpha$ , and  $\beta$  values that are now known to us (as of Feb 1983) are assembled in Table I (with the relatively less certain results in parentheses). As we have mentioned, most of the  $\pi^*$  and  $\beta$  values of the non-hydrogen-bonding and HBA solvents have "settled down" after a series of successive approximations, with additional results not likely to materially change the averages.

In the case of the amphiprotic solvents, the complications caused by self-association, type-AB hydrogen bonding, and multiple type-A and type-B interactions<sup>18</sup> have caused us to change published parameter values more often than we would care to detail. However, on the basis of results for up to 11  $\pi^*$  indicators<sup>2b</sup> and 25  $\alpha$  indicators,<sup>36</sup> we are now reasonably well satisfied with the average  $\pi^*$  and  $\alpha$  values reported in Table I for these solvents (with the proviso, however, that the average deviations for most of the  $\alpha$  values are near  $\pm 0.08$ , compared with  $\pm 0.04$  for most of the other results in Table I). The  $\beta$  values of the amphiprotic solvents are less certain (possibly  $> \pm 0.10$ ) and remain subject to change.

The table includes some important results for fluorocarbon solvents recently reported by Brady and Carr<sup>37</sup> and

by Bekarek and Jurina.<sup>38</sup> These materially increase the range of the  $\pi^*$  scale (extending the lower limit from  $-0.08$  for *n*-hexane to  $-0.40$  for the perfluoro-*n*-alkanes). Brady and Carr's  $\pi^*$  values are based on electronic spectra of 17 of the indicators used in the original formulation of the  $\pi^*$  scale (these authors also reported  $\pi^*$  values of 0.07–0.64 for some liquid methyl/phenyl silicone polymers used as chromatographic stationary phases).<sup>37</sup> Bekarek and Jurina's results<sup>38</sup> are based on electronic spectra of three of the original  $\pi^*$  indicators and the infrared spectrum of acetone. It is significant that the two investigations agree to within 0.01  $\pi^*$  unit for perfluoro-*n*-hexane, -heptane, and -octane.

The  $\pi^*$  scale is extended even further by a result recently reported by Abboud and co-workers.<sup>39</sup> On the basis of vapor-phase electronic spectra of eight of the original solvatochromic indicators, the  $\pi^*$  value of the gas phase is  $-1.1 \pm 0.1$ . The latter result and those for the perfluorocarbon solvents are likely to have important bearings on the many attempts that have recently been made to relate the empirical  $\pi^*$  scale to more fundamental measures of dipolarity and polarizability.<sup>40</sup>

We prefer the  $\beta$  values in Table I, obtained by averaging multiple (as many as 15)  $\beta_i$  results, over the "corrected  $\beta$ " ( $B_{KT}$ ) values suggested by Krygowski and co-workers<sup>41</sup> and based on a single  $\beta_i$  (from the solvatochromic comparison of 4-nitroaniline with *N,N*-diethyl-4-nitroaniline). We believe that the differences between  $\beta$  and  $B_{KT}$  are largely the results of systematic instrumental differences between the spectrophotometers at the University of Warsaw and the Naval Surface Weapons Center.

### Estimation of Additional $\pi^*$ and $\beta$ Values<sup>42</sup>

As mentioned earlier, numerous attempt have been made to relate the  $\pi^*$  parameter to more fundamental

(38) Bekarek, V.; Jurina, S. *Collect. Czech. Chem. Commun.* 1982, 47, 1060.

(39) Essfar, M.; Guiheneuf, G.; Abboud, J.-L. M. *J. Am. Chem. Soc.* 1982, 104, 6786.

(40) (a) Kolling, O. W. *Trans. Kans. Acad. Sci.* 1981, 84, 32. (b) Ehrenson, S. *J. Am. Chem. Soc.* 1981, 103, 6036. (c) Bekarek, V. *J. Phys. Chem.* 1981, 85, 722. (d) Reference 37. (e) Reference 13.

(41) Krygowski, T. M.; Milczarek, E.; Wrona, P. K. *J. Chem. Soc., Perkin Trans. 2* 1982, 1563.

(42) Note added in proof: Krygowski and co-workers have recently reported the following additional  $\beta$  values: nitromethane, 0.22; propylene carbonate, 0.40; formamide, (0.55) [Krygowski, T. M.; Reichardt, C.; Wrona, P. K.; Wyszomirska, C.; Zielkowska, U.]. These workers have also reported  $\beta$  values of mixtures of methanol with a number of solvents.

(35) Arnett, E. M.; Mitchell, E. J.; Murty, T. S. S. R. *J. Am. Chem. Soc.* 1974, 96, 3875.

(36) Taft, R. W.; et al.: paper on the  $\alpha$  scale, in preparation.

(37) (a) Brady, J. E.; Carr, P. W. *Anal. Chem.* 1982, 47, 1060. (b) Brady, J. E.; Carr, P. W. *J. Phys. Chem.* 1982, 86, 3053.

dipolarity and polarizability measures, expressed in terms of functions of the solvent refractive index ( $n$ ) and either its dipole moment ( $\mu$ ) or bulk dielectric constant ( $\epsilon$ ).<sup>40</sup> In addition to lending a measure of theoretical respectability to the empirically derived  $\pi^*$  scale, these relationships can often be used to determine new solvent  $\pi^*$  values where experimental spectral information is not available. Although characterized by Ehrenson<sup>40b</sup> and by Brady and Carr<sup>37b</sup> as "fundamentally disquieting" (in that first-order terms in the reaction-field parameter are neglected and only a second-order term used as the sole parameter and in that they lead to a  $\pi^*$  estimate of  $-0.6$  for the gas phase compared with the  $-1.1$  determined by Abboud<sup>39</sup>), separate equations for aliphatic and aromatic solvents proposed by Bekarek<sup>40c</sup> appear to give the best correlations of the available data. Bekarek's relationship for aliphatic solvents is given by eq 24. The corresponding relationship for

$$\pi^* = -0.573 + 14.65(\epsilon - 1)(n^2 - 1)/(2\epsilon + 1)(2n^2 + 1) \quad (24)$$

aromatic solvents is given by eq 25.

$$\pi^* = -0.058 + 8.08(\epsilon - 1)(n^2 - 1)/(2\epsilon + 1)(2n^2 + 1) \quad (25)$$

We have used eq 24 and 25 to estimate the  $\pi^*$  values in Table I that are enclosed in double parentheses. We suggest, however, that when new  $\pi^*$  are estimated by this method, the results be checked for consistency with known  $\pi^*$  values. Thus  $\pi^* = ((0.69))$  for phenetole in Table I accords well with  $\pi^* = 0.73$  for anisole, and  $((0.84))$  for 4-methylpyridine and  $((0.80))$  for 2,6-dimethylpyridine are consonant with  $\pi^* = 0.87$  for pyridine.

For the estimation of new  $\beta$  values, one can use correlations of structural effects on  $\beta$  by dual-substituent-parameter equations, which we have reported earlier<sup>10b</sup> for carbonyl and pyridine bases. These equations are as follows:

for  $\text{RCOCH}_3$

$$\beta = 0.40 - 0.56\sigma_I - 0.20\sigma_{R^+} \quad (26)$$

for  $\text{RCOOEt}$

$$\beta = 0.30 - 0.46\sigma_I - 0.14\sigma_{R^+} \quad (27)$$

for  $\text{RCON}(\text{CH}_3)_2$

$$\beta = 0.70 - 0.74\sigma_I - 0.072\sigma_{R^+} \quad (28)$$

for  $4\text{-X-C}_6\text{H}_4\text{CH}=\text{O}$

$$\beta = 0.44 - 0.17\sigma_I - 0.092\sigma_{R^+} \quad (29)$$

and

for  $4\text{-X-C}_5\text{H}_4\text{N}$

$$\beta = 0.63 - 0.35\sigma_I - 0.16\sigma_{R^+} \quad (30)$$

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**Registry No.** *n*-Hexane, 110-54-3; cyclohexane, 110-82-7; diisopropyl ether, 108-20-3; di-*n*-butyl ether, 142-96-1; diethyl ether, 60-29-7; dioxane, 123-91-1; tetrahydrofuran, 109-99-9; anisole, 100-66-3; tetrahydropyran, 142-68-7; dibenzyl ether, 103-50-4; diphenyl ether, 101-84-8; 1,2-dimethoxyethane, 110-71-4; di-*n*-propyl ether, 111-43-3; phenetole, 103-73-1; bis(2-methoxyethyl) ether, 111-96-6; trimethyl orthoacetate, 1445-45-0; trimethyl orthoformate, 149-73-5; 2-butanone, 78-93-3; acetone, 67-64-1; 1,1,1-trichloroacetone, 918-00-3; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; acetophenone, 98-86-2; methyl *tert*-butyl ketone, 75-97-8; benzaldehyde, 100-52-7; dimethyl- $\gamma$ -pyrone,

1004-36-0; benzophenone, 119-61-9; biacetyl, 431-03-8; 3-heptanone, 106-35-4; phenylacetone, 103-79-7; *sym*-dichloroacetone, 534-07-6; methyl isopropyl ketone, 563-80-4; *p*-methoxyacetophenone, 100-06-1; acetylferrocene, 1271-55-2; flavone, 525-82-6; *p*-nitrobenzaldehyde, 555-16-8; propionaldehyde, 123-38-6; butyraldehyde, 123-72-8; *p*-chlorobenzaldehyde, 104-88-1; *p*-methoxybenzaldehyde, 123-11-5; *p*-(dimethylamino)benzaldehyde, 100-10-7; 2-naphthaldehyde, 66-99-9; di-*tert*-butyl ketone, 815-24-7; cinnamaldehyde, 104-55-2; propiophenone, 93-55-0; 3-pentanone, 96-22-0; 2-pentanone, 107-87-9; isobutyrophenone, 611-70-1; *p*-chloroacetophenone, 99-91-2; *p*-methylacetophenone, 122-00-9; dicyclopropyl ketone, 1121-37-5; methyl cyclopropyl ketone, 765-43-5; ethyl acetate, 141-78-6; butyrolactone, 96-48-0; butyl acetate, 123-86-4; ethyl chloroacetate, 105-39-5; ethyl benzoate, 93-89-0; methyl acetate, 79-20-9; methyl formate, 107-31-3; ethyl propionate, 105-37-3; diethyl carbonate, 105-58-8; diethyl malonate, 105-53-3; ethyl acetoacetate, 141-97-9; ethyl trichloroacetate, 515-84-4; methyl trifluoroacetate, 431-47-0; propylene carbonate, 108-32-7; ethyl formate, 109-94-4; phenyl benzoate, 93-99-2; ethyl *p*-nitrobenzoate, 99-77-4; dimethyl carbonate, 616-38-6; methyl benzoate, 93-58-3; ethyl trifluoroacetate, 383-63-1; dimethylacetamide, 127-19-5; dimethylformamide, 68-12-2; *N*-methylpyrrolidone, 872-50-4; *N,N*-dimethyltrifluoroacetamide, 1547-87-1; *N,N*-dimethylchloroacetamide, 2675-89-0; tetramethylurea, 632-22-4; *N,N*-dimethyl-*p*-nitrobenzamide, 7291-01-2; *N,N*-dimethylbenzamide, 611-74-5; *N,N*-di-*n*-hexylacetamide, 16423-51-1; *N,N*-diethylacetamide, 685-91-6; *N,N*-diethylbenzamide, 1696-17-9; *N*-acetylperidine, 618-42-8; *N,N*-diphenylacetamide, 519-87-9; tetraethylurea, 1187-03-7; *N*-methylpyridone, 694-85-9; ethyl diethylcarbamate, 3553-80-8; *N,N*-diethylpropionamide, 1114-51-8; *N,N*-diphenylpropionamide, 20619-23-2; formamide, 75-12-7; acetic anhydride, 108-24-7; benzoyl fluoride, 455-32-3; propionyl fluoride, 430-71-7; benzoyl chloride, 98-88-4; benzoyl bromide, 618-32-6; acetic acid, 64-19-7; trifluoroacetic acid, 76-05-1; triethylamine, 121-44-8; tri-*n*-butylamine, 102-82-9; *N,N*-dimethylbenzylamine, 103-83-3; *N,N*-dimethylaniline, 121-69-7; triethylamine, 102-70-5; tri-*n*-propylamine, 102-69-2; *N,N*-dimethyl-*N*-propylamine, 926-63-6; *N,N*-dimethyl-*N*-cyclohexylamine, 98-94-2;  $\beta,\beta,\beta$ -trifluoroethylamine, 753-90-2; propargylamine, 2450-71-7; cyclopropylamine, 765-30-0; benzylamine, 100-46-9; *n*-butylamine, 109-73-9; quinuclidine, 100-76-5; *N*-methylimidazole, 616-47-7; 1,4-diazabicyclo[2.2.2]octane, 280-57-9; di-*n*-butylamine, 111-92-2; dimethyl sulfoxide, 67-68-5; ethyl sulfate, 540-82-9; sulfolane, 126-33-0; diphenyl sulfoxide, 945-51-7; di-*n*-butyl sulfoxide, 2168-93-6; dibenzyl sulfoxide, 621-08-9; methyl phenyl sulfoxide, 1193-82-4; methyl *p*-nitrophenyl sulfoxide, 940-12-5; diethyl sulfite, 623-81-4; di-*n*-propyl sulfite, 623-98-3; di-*n*-butyl sulfite, 626-85-7; di-*p*-tolyl sulfoxide, 1774-35-2; diisopropyl sulfoxide, 2211-89-4; tetramethylene sulfoxide, 1600-44-8; triethyl phosphate, 78-40-0; hexamethylphosphoramide, 680-31-9; tri-*n*-butyl phosphate, 126-73-8; triphenylphosphine oxide, 791-28-6; trimethyl phosphate, 512-56-1; trimethylphosphine oxide, 676-96-0; triphenyl phosphate, 115-86-6; diethoxy(trichloromethyl)phosphine oxide, 866-23-9; diethoxy(dichloromethyl)phosphine oxide, 3167-62-2; diethoxy(chloromethyl)phosphine oxide, 3167-63-3; dimethoxyphosphine oxide, 868-85-9; diethylphosphine oxide, 762-04-9; diisopropoxyphosphine oxide, 1809-20-7; dimethoxyethylphosphine oxide, 6163-75-3; diethoxymethylphosphine oxide, 683-08-9; diethoxy-(dimethylamino)phosphine oxide, 2404-03-7; tri-*n*-propylphosphine oxide, 1496-94-2; triethylphosphine oxide, 597-50-2; nitrobenzene, 98-95-3; nitromethane, 75-52-5; benzonitrile, 100-47-0; acetonitrile, 75-05-8; phenylacetone nitrile, 140-29-4; butyronitrile, 109-74-0; *p*-methoxybenzonitrile, 874-90-8;  $\beta$ -ethoxypropionitrile, 2141-62-0; *p*-(dimethylamino)benzonitrile, 1197-19-9; propionitrile, 107-12-0; pyridine, 110-86-1; 4-methylpyridine, 108-89-4; 2,6-dimethylpyridine, 108-48-5; 2,4,6-trimethylpyridine, 108-75-8; quinoline, 91-22-5; 3,5-dichloropyridine, 2457-47-8; 3-bromopyridine, 626-55-1; 4-(dimethylamino)pyridine, 1122-58-3; 2-*n*-butylpyridine, 5058-19-5; pyrimidine, 289-95-2; 2,4-dimethylpyridine, 108-47-4; 3-methylpyridine, 108-99-6; 4-methoxy pyridine, 620-08-6; toluene, 108-88-3; benzene, 71-43-2; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; *p*-xylene, 106-42-3; mesitylene, 108-67-8; *o*-dichlorobenzene, 95-50-1; iodobenzene, 591-50-4; cumene, 98-82-8; *m*-dichlorobenzene, 541-73-1; fluorobenzene, 462-06-6; *m*-xylene, 108-38-3; carbon tetrachloride, 56-

23-5; trichloroethylene, 79-01-6; 1,1,1-trichloroethane, 71-55-6; 1,2-dichloroethane, 107-06-2; methylene chloride, 75-09-2; chloroform, 67-66-3; tetrachloroethylene, 127-18-4; 1,1,2,2-tetrachloroethane, 79-34-5; *n*-butyl chloride, 109-69-3; 1,2-dibromoethane, 106-93-4; *trans*-1,2-dichloroethylene, 156-60-5; pentachloroethane, 76-01-7; methylene bromide, 74-95-3; methylene iodide, 75-11-6; perfluoro-*n*-octane, 307-34-6; perfluoro-*n*-heptane, 335-57-9; perfluorodimethyldecalin, 54471-59-9; perfluorotri-*n*-

butylamine, 311-89-7; perfluoro-*n*-hexane, 355-42-0; *tert*-butyl alcohol, 75-65-0; 2-propanol, 67-63-0; *n*-butanol, 71-36-3; ethanol, 64-17-5; methanol, 67-56-1; 2-phenylethanol, 60-12-8; ethylene glycol, 107-21-1; benzyl alcohol, 100-51-6; 2-chloroethanol, 107-07-3; water, 7732-18-5; *n*-propanol, 71-23-8; trifluoroethanol, 75-89-8; hexafluoroisopropanol, 920-66-1; 2-fluoroethanol, 371-62-0; 2-methoxyethanol, 109-86-4; pyridine *N*-oxide, 694-59-7; 5-fluoroindole, 399-52-0; *n*-heptane, 142-82-5.

## Reaction of Triflates with Potassium Diethyl Phosphite. Formation of Phosphate Esters

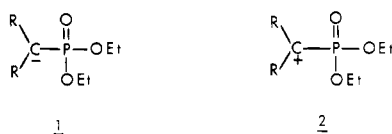
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Phenyl triflate and substituted analogues react with potassium diethyl phosphite in liquid ammonia to form aryl diethyl phosphate esters. The reaction formally involves loss of trifluoromethanesulfinate ion from the triflate and concomitant oxidation of phosphorus to the phosphate stage. Preliminary data suggest that, in a series of triflates, reactivity follows the order aryl > cyclohexenyl > cyclopropyl > alkyl. Studies on aryl triflates with added labeled phenoxide rule out a mechanism involving free phenoxide ion, i.e., displacement of phenoxide by nucleophilic attack of diethyl phosphite ion on sulfur followed by phosphorylation of displaced phenoxide. Three potential mechanisms, including one involving initial attack of phosphorus at sulfur, a biphilic insertion mechanism, and one involving nucleophilic attack on oxygen, are suggested, all of which could account for these observations.

The diethylphosphonate group is a well-known carbanion-stabilizing substituent.<sup>1</sup> This feature permits facile generation of anions of general structure 1. Recently we



have generated carbocations of general structure 2 by the solvolytic route.<sup>2</sup> In view of the unexpected ease of generation of 2, we wanted to evaluate the electronic properties, both conjugative and inductive, of the diethyl phosphonate group. We therefore wanted to introduce this group onto an aromatic nucleus for potential measurement of  $\sigma^+$  values and also for potential measurement of effects on benzylic-type free radicals.

Various methods for substitution of PO(OEt)<sub>2</sub> for halogen on an aromatic ring have been developed.<sup>3-6</sup> Since the requisite aryl iodides and bromides necessary for the transformation shown below are not always readily

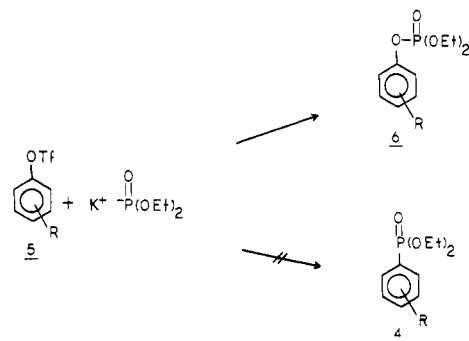


available, we sought to develop a method starting with the more accessible phenols. In principle, conversion of a

phenol to the aryl triflate followed by displacement of the triflate leaving group with the anion of diethyl phosphite would lead to the aryl phosphonate 4. It was hoped that the displacement of the excellent nucleofugic triflate group could be accomplished by either an S<sub>RN</sub>1 mechanism,<sup>7</sup> an S<sub>N</sub>Ar process,<sup>8</sup> or possibly even a direct displacement of triflate.<sup>9</sup> Reported here are the results of a study of the reaction of aryl triflates with potassium diethyl phosphite in liquid ammonia.

### Results and Discussion

A variety of phenols were converted to the corresponding triflates 5. These were added to potassium diethyl phosphite in liquid ammonia at -33 °C. Under these conditions, even in the dark, the triflates were all consumed. However, none of the aryl phosphonates 4 were



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(9) The possibility of such a process occurring in nucleophilic vinylic substitution has been discussed. See: Rappoport, Z. *Acc. Chem. Res.* 1981, 14, 7-15.