

eq ES-1 holds, where  $x_A^i$  stands for the concentration of

$$\phi_i = (\Delta^0 - \Delta^i) / \Delta^i = K_1 x_A^i + K_2 K_3 (x_A^i)^2 \quad (\text{ES-1})$$

monomeric alcohol present in the solution. Since neither  $K_2$  nor the  $x_A^i$  are known off hand, an iterative minimax search for the optimal values of the constants is carried out. We have developed a program for the HP-41C programmable calculator which allows the determination of

these constants from the experimental absorptivities  $\Delta^i$  and the gross mole-fraction of the alcohol. The experimental values given in this work are the average of four to eight runs, each of them involving 12 to 25 solutions (i.e.,  $i = 12-25$ ).

**Supplementary Material Available:** Table of experimental  $x_i$  and  $\phi_i$  values and listing of the programs (7 pages). Ordering information is given on any current masthead page.

## Linear Solvation Energy Relationships. 14. Additions to and Correlations with the $\beta$ Scale of Hydrogen Bond Acceptor Basicities

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Received May 3, 1982

Existing literature data and new results are used with correlations reported earlier, as well as some new correlations first reported here, to determine  $\beta$  values of 90 additional liquid and solid hydrogen bond acceptor bases containing various types of functional groups as acceptor sites. Differences between "family independent (FI)" and "family dependent (FD)" correlations with  $\beta$  are demonstrated.

In earlier papers on the subject of linear solvation energy relationships (LSER's), we used a "solvatochromic comparison method" to unravel multiple solvent effects on many types of properties and rationalize them in terms of linear combinations of dependences on three indexes of solvent properties (the solvatochromic parameters). The  $\pi^*$  scale is an index of solvent dipolarity/polarizability which measures the ability of the medium to stabilize a charge or a dipole by virtue of its dielectric effect.<sup>1-4</sup> The  $\alpha$  scale of solvent hydrogen bond donor (HBD) acidities describes the solvent's ability to donate a proton in a solvent to solute hydrogen bond.<sup>1,5-7</sup> The  $\beta$  scale of hydrogen bond acceptor (HBA) 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.<sup>10</sup> Rather than being based on solvent effects on single indicators, as has been the case for most earlier solvent property scales,<sup>12</sup> the solvatochromic pa-

rameters were arrived at by averaging normalized solvent effects on diverse properties of many types of indicators.

The solvatochromic parameters were intended for use in linear solvation energy relationships of the general form of eq 1 where  $\delta$ , a "polarizability correction term", is 0.0

$$\text{XYZ} = \text{XYZ}_0 + s(\pi^* + d\delta) + a\alpha + b\beta \quad (1)$$

for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents.<sup>13a</sup> Numerous relatively precise LSER's have been reported wherein the XYZ term in eq 1 has been the logarithm of a reaction rate or equilibrium constant, a fluorescence lifetime or a GLC partition coefficient, a position or intensity of maximal absorption in an NMR, ESR, IR, or UV/visible absorption or fluorescence spectrum, an NMR coupling constant, or a free energy or enthalpy of solution or of transfer between solvents.

In practice it has proven quite difficult to disentangle the multiple solvent effects when all four solvatochromic parameters influenced the XYZ (primarily because of complications by type AB hydrogen bonding when both solvent and solute are amphiprotic).<sup>13b</sup> By judicious choices of solvents and/or reactants or indicators, however, it has usually been possible to exclude one or more of the terms in eq 1 and reduce it to a more manageable form.<sup>14</sup>

Thus, if XYZ is  $\nu_{\text{max}}$  or the transition energy of a  $\pi \rightarrow \pi^*$  electronic spectral transition, the  $d$  term is zero. For other properties, if consideration is limited to nonchlorinated aliphatic solvents, the  $\delta$  parameter is zero. In either case the  $d\delta$  term drops out. If the indicators or reactants are nonprotonic (and non Lewis acids),<sup>11</sup>  $b$  equals zero, and the  $b\beta$  term drops out. With protonic or Lewis acid reactants or indicators, correlations have usually been restricted to nonprotonic solvents for which the  $\alpha$  param-

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(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. *J. Org. Magn. Reson.* 1980, 14, 485.

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(14) See, however, correlations with  $\pi^*$ ,  $\alpha$ , and  $\beta$  in: (a) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *Chem. Phys. Lett.* 1981, 77, 69. (b) Kamlet, M. J.; Dickinson, C.; Taft, R. W. *J. Chem. Soc., Perkin Trans. 2*, 1981, 353.

eter equals zero, so that the  $\alpha\alpha$  term drops out. Most of the correlations which we have so far reported have been with the  $\pi^*$  parameter alone (with or without the  $d\delta$  correction),<sup>2-4,13a,15</sup> with  $\beta$  alone,<sup>10</sup> with  $\pi^*$  and  $\alpha$ ,<sup>5,6,11b</sup> and with  $\pi^*$  and  $\beta$ .<sup>9,11b,14</sup>

In a recent review article,<sup>1</sup> we listed  $\pi^*$  values for 89 solvents of all types,  $\alpha$  values for 15 HBD solvents, and  $\beta$  values for 61 HBA bases, most of which were liquid but which also included some solid materials dissolved in non-HBA solvents. In the present paper we use existing literature data, together with some correlation equations reported earlier, as well as some new correlations first reported here, to determine  $\beta$  values of 90 additional liquid and solid HBA bases containing various types of functional groups as hydrogen bond acceptor sites. We include only those compounds for which it was possible to average  $\beta_i$  values from two or more independently determined XYZ's and wherein the average deviation from the mean was less than 0.04  $\beta$  unit.

## Results and Discussion

**Correlation Equations.** LSER's so far reported with the  $\beta$  scale have been of two general types: (a) correlations wherein the property studied is proportional to or linear with  $\beta$  for all HBA bases considered together; (b) 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 (e.g., only double bonded oxygen bases, only single bonded oxygen bases, or only pyridine bases). In the latter instances, regression lines with  $\beta$  for the different families of HBA bases were usually (but not always) nearly parallel.

The properties used in the initial construction of the  $\beta$  scale were of the first general type. Thus, we have reported<sup>8a</sup> that formation constants of 4-fluorophenol (4-FP) complexes with HBA bases of all types in  $\text{CCl}_4$  solvent (which were the basis for the earlier  $\text{p}K_{\text{HB}}$  scale)<sup>16,17</sup> are related to  $\beta$  through eq 2. Limiting  $^{19}\text{F}$  NMR shifts for

$$\log K_f(4\text{-FP:HBA}) = \text{p}K_{\text{HB}} = 4.40\beta - 1.00 \quad (2)$$

$$^{19}\text{F NMR } \Delta(4\text{-FP:HBA}) = 3.82\beta \quad (3)$$

$$\log K_f(\text{phenol:HBA}) = 4.31\beta - 1.05 \quad (4)$$

the same complexes in  $\text{CCl}_4$ ,<sup>17,18</sup> are related to  $\beta$  through eq 3. Formation constants for phenol complexes with HBA bases are linear with  $\beta$  according to eq 4.

More recently,<sup>10</sup> we have used infrared  $\Delta\nu$  values (free minus hydrogen bonded) of the O-H stretching frequencies of the phenol complexes with the HBA bases in  $\text{CCl}_4$  to amend and expand the  $\beta$  scale. This is a property of the second type, and the different families of bases conformed to separate regression lines. Thus, we reported the following correlations: (a) for double bonded oxygen bases:

$$\Delta\nu(\text{O-H, phenol:HBA}) = -37.1 + 487\beta \text{ cm}^{-1} \quad (5a)$$

(b) for single bonded oxygen bases:

$$\Delta\nu(\text{O-H, phenol:HBA}) = 67.1 + 436\beta \text{ cm}^{-1} \quad (5b)$$

and (c) for pyridine bases:

$$\Delta\nu(\text{O-H, phenol:HBA}) = 180.2 + 473\beta \text{ cm}^{-1} \quad (5c)$$

It was suggested that the nonlinearity of  $\Delta\nu$  with  $\beta$  between families of HBA bases was because of different geometries

of the hydrogen bonds (angles between axes of vibrating O-H bonds and directions of acceptor dipoles) and differing orbital hybridizations on the acceptor atoms.

**$\beta$  Values of Carbonyl Bases.** In Table I we have assembled 47 new sets of  $\beta_i$  and  $\beta_{\text{av}}$  results, as determined from seven diverse properties. The carbonyl bases in Table I include 23 aldehydes and ketones, 12 carboxamides, 8 carboxylic acid esters, and 4 carbonyl halides. The values of  $\beta_1$  and  $\beta_2$  in Table I were back-calculated through eq 2 and 3 by using the  $\log K_f(4\text{-FP:HBA})$  and  $^{19}\text{F}$  NMR  $\Delta(4\text{-FP:HBA})$  data of Taft and co-workers.<sup>16-18</sup> The  $\log K_f(\text{phenol:HBA})$  data of Gramstad and co-workers<sup>19,20</sup> were used with regression eq 4 to obtain the  $\beta_3$  values. The  $\Delta\nu(\text{O-H, phenol:HBA})$  results of the Gramstad group<sup>19,20</sup> were used to back-calculate values of  $\beta_4$  from eq 5a.

Two interesting and hitherto unpublished correlations were employed to arrive at the next pair of  $\beta_i$  sets. Laurence and co-workers have measured free energies and enthalpies of formation of iodine complexes with a large number of HBA bases in heptane at 25 °C<sup>21,22a</sup> and have found<sup>22b</sup> that, if consideration is limited to the carbonyl bases only, both sets of properties for these Lewis acid-base complexes are nicely linear with  $\beta$ . According to our present calculations, the regression equations (considering only the HBA bases whose  $\beta$  values were known earlier) are given by eq 6 and 7. The new  $\beta_5$  and  $\beta_6$  results in

$$\Delta G_f(\text{I}_2:\text{HBA}) = 2.45 - 5.21\beta \text{ kcal/mol} \quad (6)$$

$n = 15$ ,  $r$  (the correlation coefficient) =

$$0.989, \text{ sd (the standard deviation)} = 0.11 \text{ kcal/mol}$$

$$\Delta H_f(\text{I}_2:\text{HBA}) = -0.47 - 7.54\beta \text{ kcal/mol} \quad (7)$$

$$n = 16, r = 0.973, \text{ sd} = 0.26 \text{ kcal/mol}$$

Table I were back-calculated from additional data of Laurence and co-workers with eq 6 and 7.

Finally, the  $\beta_7$  values in Table I were determined from the data of Shorter and co-workers<sup>23</sup> with a previously reported<sup>10</sup> regression equation for  $\Delta\nu(\text{O-D})$  values (gas-phase minus solution) of the O-D stretching frequencies of methan[<sup>2</sup>H]ol in the pure double bonded oxygen base solvents (eq 8).

$$\Delta\nu(\text{O-D, MeOD:HBA}) = -6.41 + 240\beta \text{ cm}^{-1} \quad (8)$$

**Phosphine Oxide, Sulfoxide, Amine N-Oxide, and Nitrile Bases.** The same correlation equations and data sources as before were used to arrive at the  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  values for the 26 phosphine oxide, sulfoxide, amine N-oxide, and nitrile bases in Table II. Unlike the earlier instances, however, previously unreported correlations and series of successive approximations were used to determine the  $\beta_4$  values from the  $\Delta\nu(\text{O-H, phenol:HBA})$  results. This was because, whereas Kamlet, Solomonovici, and Taft<sup>10</sup> had considered P=O and S=O bases together with C=O

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Table I.  $\beta$  Values of Some Hydrogen Bond Acceptor Bases. Double Bonded Oxygen Bases

no. <sup>g</sup>	HBA base	$\beta_1$ , <sup>a</sup> eq 2	$\beta_2$ , <sup>b</sup> eq 3	$\beta_3$ , <sup>c</sup> eq 4	$\beta_4$ , <sup>d</sup> eq 5a	$\beta_5$ , <sup>e</sup> eq 6	$\beta_6$ , <sup>e</sup> eq 7	$\beta_7$ , <sup>f</sup> eq 8	$\beta_{av}$
Aldehydes and Ketones									
139	<i>sym</i> -dichloroacetone	0.34		0.34	0.33				0.34
76	benzophenone	0.44		0.45	0.46	0.45	0.40		0.44
65	methyl <i>tert</i> -butyl ketone	0.46		0.47	0.49	0.49	0.51	0.43	0.48
140	methyl isopropyl ketone	0.46		0.47	0.49	0.48	0.51	0.45	0.48
141	<i>p</i> -methoxyacetophenone	0.53	0.55			0.54			0.54
142	acetylferrocene	0.60	0.56						0.58
143	flavone	0.68	0.64						0.66
71	2,6-dimethyl- $\gamma$ -pyrone	0.80	0.78	0.78	0.79				0.79
144	<i>p</i> -nitrobenzaldehyde	0.31		0.32	0.32				0.32
145	propionaldehyde	0.39		0.40	0.42				0.40
146	butyraldehyde	0.40		0.41	0.42	0.39	0.43		0.41
147	<i>p</i> -chlorobenzaldehyde	0.39		0.41	0.45				0.42
148	<i>p</i> -methoxybenzaldehyde	0.48	0.50						0.49
149	<i>p</i> -dimethylaminobenzaldehyde	0.58	0.61	0.55	0.61				0.59
150	2-naphthaldehyde			0.41	0.44				0.43
151	di- <i>tert</i> -butyl ketone			0.47	0.48				0.48
152	cinnamaldehyde			0.50	0.56				0.53
153	propiophenone				0.43	0.44	0.42		0.43
154	3-pentanone					0.47	0.43	0.44	0.45
155	2-pentanone			0.50	0.50			0.49	0.50
156	isobutyrophenone				0.42	0.43	0.40		0.42
157	<i>p</i> -chloroacetophenone				0.47	0.45	0.45		0.46
158	<i>p</i> -methylacetophenone				0.52	0.51	0.51		0.51
Amides, Carbamates, and Urea									
159	<i>N,N</i> -dimethyl- <i>p</i> -nitrobenzamide	0.60	0.58	0.63	0.61				0.61
160	<i>N,N</i> -dimethylbenzamide	0.73	0.77	0.71	0.70	0.71	0.71		0.72
161	<i>N,N</i> -di- <i>n</i> -hexylacetamide			0.77	0.78				0.77
162	<i>N,N</i> -diethylacetamide	0.78		0.77	0.77	0.80	0.76		0.78
163	<i>N,N</i> -diethylbenzamide			0.70	0.69				0.70
164	<i>N</i> -acetylpiperidine			0.73	0.73				0.73
165	<i>N,N</i> -diphenylacetamide			0.65	0.63				0.64
166	tetraethylurea				0.74	0.74	0.66		0.71
167	<i>N</i> -methylpyridone	0.77	0.78	0.78	0.78				0.78
168	ethyl <i>N,N</i> -diethylcarbamate	0.63	0.66						0.65
169	<i>N,N</i> -diethylpropionamide			0.74	0.75				0.75
170	<i>N,N</i> -diphenylpropionamide			0.63	0.59				0.61
Esters									
171	phenyl benzoate			0.40	0.37				0.39
172	ethyl <i>p</i> -nitrobenzoate			0.41	0.38				0.40
96	ethyl trichloroacetate				0.22	0.31	0.23		0.25
38	ethyl formate				0.33	0.39	0.35		0.36
173	dimethyl carbonate				0.38	0.41	0.35		0.38
174	methyl benzoate				0.40	0.41	0.37		0.39
85	diethyl carbonate				0.40	0.42	0.40	0.38	0.40
175	ethyl trifluoroacetate				0.19	0.21	0.16		0.19
Acid Halides									
176	benzoyl fluoride	0.16		0.17	0.14				0.16
177	propionyl fluoride	0.20		0.21	0.18				0.20
178	benzoyl chloride				0.19	0.20	0.21		0.20
179	benzoyl bromide					0.16	0.16		0.16

<sup>a</sup> References 16 and 17. <sup>b</sup> References 17 and 18. <sup>c</sup> Reference 19. <sup>d</sup> References 19–21. <sup>e</sup> References 21 and 22 and unpublished results of Laurance. <sup>f</sup> Reference 23. <sup>g</sup> HBA base numbering is the same in all papers of this series.

bases in deriving eq 5a for double bonded oxygen bases, Gramstad<sup>19b</sup> has shown his infrared  $\Delta\nu$  measurements to be sufficiently precise to distinguish between phosphine oxide, sulfoxide, and carbonyl bases. For this reason, we have considered these subfamilies separately and have correlated the data of Gramstad<sup>19,20</sup> with a  $\beta$  set comprising earlier known values together with preliminary values obtained by averaging the  $\beta_1$ – $\beta_3$  terms in Table II. In this manner we have arrived at regression eq 5d for phosphine

$$\Delta\nu(\text{phenol:O=PR}_3) = -199.6 + 671\beta \text{ cm}^{-1} \quad (5d)$$

$$n = 16, r = 0.989, \text{sd} = 13.3 \text{ cm}^{-1}$$

$$\Delta\nu(\text{phenol:O=SR}_2) = -120.6 + 614\beta \text{ cm}^{-1} \quad (5e)$$

$$n = 9, r = 0.998, \text{sd} = 7.0 \text{ cm}^{-1}$$

oxide bases and eq 5e for sulfoxide bases. Equations 5d and 5e were then used to back-calculate the  $\beta_4$  values for the phosphine oxides and sulfoxides.

The last two sets of  $\beta_i$  values in Table II were obtained from LSER's involving (a) infrared stretching frequency shifts (free Lewis acid minus complex with the HBA base in  $\text{CCl}_4$ ) of the carbon-iodine bond of cyanogen iodide and (b) logarithms of formation constants of complexes of the Lewis acid  $\text{I}_2$  with the HBA bases in  $\text{CCl}_4$ . As before,  $\beta_1$ – $\beta_4$  values were averaged to obtain the preliminary  $\beta$  set, which was then used to correlate the data of Laurence and co-workers<sup>22</sup> and those of Gramstad and Snaprud.<sup>24</sup> The linear regressions are given by eq 9 and 10 (an obviously

$$\Delta\nu(\text{N}\equiv\text{C}-\text{I}:\text{O}=\text{PR}_3) = 20.0 + 57.8\beta \text{ cm}^{-1} \quad (9)$$

$$n = 6, r = 0.999, \text{sd} = 1.0 \text{ cm}^{-1}$$

$$\log K_f(\text{I}_2:\text{O}=\text{PR}_3) = -3.55 + 4.96\beta \quad (10)$$

$$n = 6, r = 0.982, \text{sd} = 0.13$$

out-of-line point for triethyl phosphate having been excluded from the latter correlation). Equations 9 and 10 were then used with the same data to back calculate the  $\beta_5$  and  $\beta_6$  values in Table II.

**Amine and Pyridine Bases.** New  $\beta_i$  and  $\beta_{av}$  values for 13 primary, secondary, and tertiary amines and 5 pyridine and pyrimidine bases are assembled in Table III. Again the  $\beta_1$ - $\beta_3$  values for the amines and the  $\beta_1$  and  $\beta_2$  values for the pyridines were determined from the same regression equations and data sources as before. The  $\beta_4$  values for the amines were calculated from formation constants of the amine/chloroform complexes in cyclohexane at 35 °C, as reported by Takayama, Fujita, and Nakajima.<sup>25</sup> These workers had pointed out that when  $\log K_f$  values for these complexes were plotted against  $\text{p}K_{\text{HB}}$  (which, as we have mentioned earlier, is linear with  $\beta$ ), amines, ethers, and double bonded oxygen bases clearly conform to separate (but nonparallel) regression lines. In a future paper, we shall show, however, that this seeming separation into families is an artifact, caused by a multiple dependence of  $\log K_f(\text{CHCl}_3:\text{HBA})$  on both the basicity and the dipole moment of the HBA base, and that HBA bases from all three families conform to the same multiple linear regression equations with  $\beta$  and  $\mu$  or with  $\beta$  and  $\pi^*$ . If the amines are considered alone, however, correlation eq 11,

$$\log K_f(\text{CHCl}_3:\text{NR}_3) = -2.52 + 3.10\beta \quad (11)$$

$$n = 10, r = 0.909, \text{sd} = 0.12$$

obtained as before by using a preliminary  $\beta_1$ - $\beta_3$  set, is sufficiently precise to back-calculate the  $\beta_4$  values. For the pyridine bases, the  $\Delta\nu(\text{O}-\text{H}, \text{phenol}:\text{HBA})$  correlation reported earlier<sup>10</sup> (eq 5c) was used to back-calculate the  $\beta_3$  values from the data of Laurence and co-workers.<sup>22</sup>

When the present findings are combined with earlier results,<sup>1,10</sup>  $\beta$  values are now available for more than 150 HBA bases. These include 29 aldehydes and ketones, 17 carboxamides and ureas, 14 carboxylic acid esters, 4 acyl halides, 10 ethers, 16 P=O compounds, 12 S=O compounds, 5 nitriles, 15 pyridines and pyrimidines, 16  $\text{sp}^3$ -hybridized amines, and 10 ROH compounds (most of the latter still being relatively uncertain).<sup>8a,26</sup>

**Structural Effects on  $\beta$  Values.** A dual substituent parameter (DSP) equation of the form shown in eq 12 has

$$\text{basicity property (BP)} = \text{BP}_0 + \rho_I\sigma_I + \rho_R\sigma_{R^+} \quad (12)$$

previously been used to correlate structural effects on  $\text{p}K_{\text{HB}}$ <sup>27</sup> and  $\Delta G_f(\text{I}_2:\text{HBA})$ <sup>21</sup> for carbonyl compounds. The available  $\beta$  values for three series of carbonyl bases, X-CO-R, are given in Table IV. In these series, X is a variable substituent and R is the fixed substituent,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5\text{O}$ , or  $(\text{CH}_3)_2\text{N}$ . The  $\beta$  values are very well correlated by eq 12 by using for the X substituent the  $\sigma_I$  values reported by Fujio, McIvor, and Taft<sup>28</sup> and the  $\sigma_{R^+}$  values reported by Ehrenson, Brownlee, and Taft,<sup>29</sup> except that

for  $\pi$ -electron acceptor substituents the  $\sigma_{R^+}$  value is taken as zero, as suggested by recent evidence.<sup>30</sup> The correlation equations are as follows: for R =  $\text{CH}_3$ , eq 13a, with  $n = 10$ ,  $r = 0.987$ , and  $\lambda (= \rho_R/\rho_I) = 0.36$

$$\beta = 0.40 - 0.56\sigma_I - 0.20\sigma_{R^+} \quad (13a)$$

for R =  $\text{C}_2\text{H}_5\text{O}$ , eq 13b, with  $n = 7$ ,  $r = 0.995$ , and  $\lambda = 0.30$

$$\beta = 0.30 - 0.46\sigma_I - 0.14\sigma_{R^+} \quad (13b)$$

and for R =  $(\text{CH}_3)_2\text{N}$ , eq 13c, with  $n = 6$ ,  $r = 0.994$ , and  $\lambda = 0.10$

$$\beta = 0.70 - 0.74\sigma_I - 0.072\sigma_{R^+} \quad (13c)$$

These correlation equations indicate that the value of  $\beta$  is increased by both conjugative (R) and field/inductive (F) electron release by the substituent X. The common R substituent modulates the relative sensitivity of the  $\beta$  value to the R and F effects. As the  $\pi$ -donor ability of R increases from  $\text{CH}_3$  to  $\text{C}_2\text{H}_5\text{O}$  to  $(\text{CH}_3)_2\text{N}$ , i.e., as given by its  $\sigma_{R^+}$  value, the magnitude of the  $\rho_R$  value as well as the ratio  $\rho_R/\rho_I = \lambda$  decreases; that is,  $\pi$ -electron release by R decreases the effect on  $\beta$  of  $\pi$ -electron release by X (a saturation effect). Similar behavior is observed in the phosphine oxide and sulfoxide series.

The DSP eq 12 also correlates (with average deviations of  $\pm 0.01$ ) the  $\beta$  values of 4- $\text{XC}_6\text{H}_4\text{CH}=\text{O}$  and 4- $\text{XC}_6\text{H}_5\text{N}$ . The correlation equations are as follows: for the benzaldehydes, eq 14a, with  $n = 5$ ,  $r = 0.991$ , and  $\lambda = 0.54$ ,

$$\beta = 0.44 - 0.17\sigma_I - 0.092\sigma_{R^+} \quad (14a)$$

and for the pyridines, eq 14b, with  $n = 6$ ,  $r = 0.994$ ,  $\lambda = 0.45$

$$\beta = 0.63 - 0.35\sigma_I - 0.16\sigma_{R^+} \quad (14b)$$

**Some Correlations with the  $\beta$  Scale.** As was mentioned earlier, two general types of situations have been encountered in attempts at correlations with the  $\beta$  scale: (a) results for all HBA bases conformed to the same regression line with  $\beta$ ; (b) linear regression with  $\beta$  was observed within families of HBA bases, but not between families. Included among the examples of the first type which have thus far been reported are electronic spectral  $\Delta\Delta\nu$  values (enhanced solvatochromic shifts attributable to hydrogen bonding) for a number of HBD indicators,<sup>1,8,9</sup>  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{119}\text{Sn}$  NMR shifts and coupling constants for various types of HBD and nonprotonic Lewis acid indicators,<sup>1,11b,31</sup> and  $\log K_{\text{assn}}$  and  $\Delta G_f$  values for complexes of HBA bases with several types of HBD acids.<sup>1,2a</sup> In addition, a number of correlations have shown dependences of  $\Delta G_f(\text{HBA}:\text{HBD})$  on linear combinations of the  $\beta$  and  $\pi^*$  parameters or on  $\beta$  and the dipole moment,  $\mu$ , of the HBA base.<sup>32</sup>

A further example of the first type of correlation is given by the  $^{19}\text{F}$  NMR  $\Delta$  values of 5-fluoroindole complexes with HBA bases. Shifts for the complexes relative to the free acid in  $\text{CCl}_4$  (with 0.01 M *N*-methyl-5-fluoroindole as the internal standard) reported by Mitsky, Joris, and Taft<sup>33</sup> are plotted against  $\beta$  values in Figure 1, where it is seen that the results for C=O, S=O, P=O, ROR, pyridine, and  $\text{R}_3\text{N}$  bases are very clearly colinear. The regression

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Table II.  $\beta$  Values of Some Phosphine Oxide, Sulfoxide, Amine *N*-Oxide, and Nitrile HBA Bases

no.	HBA base	$\beta_1$ , <sup>a</sup> eq 2	$\beta_2$ , <sup>b</sup> eq 3	$\beta_3$ , <sup>c</sup> eq 4	$\beta_4$ , <sup>e,f</sup> eq 5d	$\beta_5$ , <sup>d</sup> eq 9	$\beta_6$ , <sup>e</sup> eq 10	$\beta_{av}$
Phosphine Oxides								
180	triphenyl phosphate	0.62		0.62	0.61			0.62
181	diethoxy(trichloromethyl)phosphine oxide	0.68		0.68	0.68			0.68
182	diethoxy(dichloromethyl)phosphine oxide	0.74		0.74	0.71	0.73	0.76	0.74
183	diethoxy(chloromethyl)phosphine oxide	0.81		0.80	0.78	0.79	0.77	0.79
184	dimethoxyphosphine oxide	0.74		0.73	0.74			0.74
185	diethoxyphosphine oxide	0.77		0.76	0.76			0.76
186	diisopropoxyphosphine oxide			0.80	0.79			0.80
187	dimethoxyethylphosphine oxide	0.78		0.83	0.83			0.81
188	diethoxymethylphosphine oxide	0.86		0.84	0.83			0.84
70	trimethyl phosphate	0.77	0.72	0.77	0.77	0.80	0.76	0.77
189	diethoxy(dimethylamino)phosphine oxide	0.89		0.87	0.89		0.85	0.88
190	tri- <i>n</i> -propylphosphine oxide	1.05		1.03	1.04			1.04
191	triethylphosphine oxide	1.05		1.03	1.06	1.06	1.06	1.05
Sulfoxides								
192	dibenzyl sulfoxide	0.75		0.73	0.73 <sup>g</sup>			0.74
193	methyl phenyl sulfoxide	0.72	0.70					0.71
194	methyl <i>p</i> -nitrophenyl sulfoxide	0.59	0.61					0.60
195	diethyl sulfite	0.45		0.45	0.45 <sup>g</sup>			0.45
196	di- <i>n</i> -propyl sulfite			0.44	0.45 <sup>g</sup>			0.45
197	di- <i>n</i> -butyl sulfite			0.46	0.46 <sup>g</sup>			0.46
198	di- <i>p</i> -tolyl sulfoxide			0.71	0.72 <sup>g</sup>			0.72
199	diisopropyl sulfoxide			0.78	0.78 <sup>g</sup>			0.78
200	tetramethylene sulfoxide			0.79	0.80 <sup>g</sup>			0.80
Amine <i>N</i> -Oxide								
221	pyridine <i>N</i> -oxide	0.85		0.84				0.85
Nitriles								
222	<i>p</i> -methoxybenzoxitrile	0.45	0.48					0.46
223	$\beta$ -ethoxypropionitrile	0.47	0.49					0.48
224	<i>p</i> -(dimethylamino)benzoxitrile	0.54	0.51					0.53

<sup>a</sup> References 16 and 17. <sup>b</sup> References 17 and 18. <sup>c</sup> Reference 20e. <sup>d</sup> Reference 22. <sup>e</sup> Reference 22 and: Gramstad, T. *Acta Chem. Scand.* 1962, 16, 99. <sup>f</sup> Gramstad, T. *Spectrochim. Acta* 1963, 18, 829. <sup>g</sup> Equation 5e.

Table III.  $\beta$  Values of Some Amine and Pyridine HBA Bases

no.	HBA base	$\beta_1$ , <sup>a</sup> eq 2	$\beta_2$ , <sup>b</sup> eq 3	$\beta_3$ , <sup>c</sup> eq 4	$\beta_4$ , <sup>d</sup> eq 11	$\beta_{av}$
Amines						
225	triallylamine	0.52	0.55	0.54		0.54
226	tri- <i>n</i> -propylamine	0.56		0.59	0.53	0.56
227	<i>N,N</i> -dimethyl- <i>N</i> -propylamine	0.68	0.66		0.70	0.68
228	<i>N,N</i> -dimethyl- <i>N</i> -cyclohexylamine	0.70	0.71	0.70	0.73	0.71
229	$\beta,\beta,\beta$ -trifluoroethylamine	0.36	0.38			0.37
230	propargylamine	0.56	0.57			0.57
231	cyclopropylamine	0.60	0.60			0.60
232	benzylamine	0.63	0.63	0.62	0.65	0.63
233	<i>n</i> -butylamine	0.71		0.70	0.74	0.72
234	quinuclidine	0.83	0.77		0.80	0.80
235	<i>N</i> -methylimidazole	0.80	0.84			0.82
236	1,4-diazabicyclo[2.2.2]octane (Dabco)	0.73	0.72			0.73
237	di- <i>n</i> -butylamine			0.69	0.71	0.70
Pyridine and Pyrimidine Bases						
238	2- <i>n</i> -butylpyridine	0.65	0.66			0.66
239	pyrimidine	0.47	0.48			0.48
240	3-methylpyridine	0.68		0.67 <sup>e</sup>		0.68
241	2,4-dimethylpyridine	0.72		0.76 <sup>e</sup>		0.74
242	4-methoxypyridine	0.71	0.73			0.72

<sup>a</sup> References 16 and 17. <sup>b</sup> References 17 and 18. <sup>c</sup> Reference 20e. <sup>d</sup> Reference 25. <sup>e</sup> Equation 5c; ref 22.

equation for 15 HBA bases (plus one zero/zero point representing the result in pure CCl<sub>4</sub>) is given by eq 15.

$$^{19}\text{F NMR } \Delta(5\text{-fluoroindole:HBA}) = -0.06 + 2.04\beta \text{ ppm} \quad (15)$$

$$r = 0.992, \text{ sd} = 0.06 \text{ ppm}$$

That the intercept in eq 15 is no larger than the standard deviation suggests that the correlation does, indeed, reflect a direct proportionality (as was observed earlier for the <sup>19</sup>F

NMR  $\Delta$  of 4-fluorophenol).<sup>8a</sup> Because the present study has allowed the inclusion of additional data points, eq 12 differs slightly from the regression equation reported earlier for this property.<sup>11b</sup> We shall refer to correlations of the above type as "family independent (FI)".

Among reported examples of the second type of correlation, which we shall refer to as "family dependent (FD)", are infrared stretching frequency shifts,  $\Delta\nu(\text{O-H, free minus hydrogen bonded})$ , of phenol, 4-fluorophenol, and methanol (some of which were used to obtain the  $\beta_i$  values

Table IV. Structural Effects on  $\beta$  Values of Carbonyl Bases

substituent	$\sigma_I$	$\sigma_{R^+}$	RCOOEt		RCONMe <sub>2</sub>		RCOMe	
			no. <sup>a</sup>	$\beta$	no. <sup>a</sup>	$\beta$	no. <sup>a</sup>	$\beta$
CF <sub>3</sub>	0.43	0.00	175	0.19	<i>a</i>	0.41	<i>b</i>	0.18
Cl	0.46	-0.36	<i>a</i>	0.23	<i>a</i>	0.36	<i>a</i>	0.23
Br	0.44	-0.30					<i>a</i>	0.24
H	0.00	0.00	38	0.36	25	0.69	<i>a</i>	0.38
MeO	0.25	-1.02	<i>a</i>	0.41			52	0.42
EtO	0.25	-1.05			<i>a</i>	0.69	11	0.45
Me	-0.04	-0.25	11	0.45	23	0.76	18	0.48
Et	-0.05	-0.22	<i>a</i>	0.46			16	0.48
Me <sub>2</sub> N	0.06	-1.75	<i>a</i>	0.61	75	0.78	23	0.76
F	0.50	-0.57					177 <sup>c</sup>	0.20 <sup>c</sup>

<sup>a</sup> Where number is not given,  $\beta$  is estimated from eq 6 and from either results reported in ref 21 or unpublished results by the same authors. These results were not included in Table I because a second corroborating  $\beta_i$  was not available. <sup>b</sup> Estimated from  $pK_{HB}$  and eq 2. <sup>c</sup> Estimated from eq 2 and the  $pK_{HB}$  of propionyl fluoride (which was assumed to be the same as for acetyl fluoride).

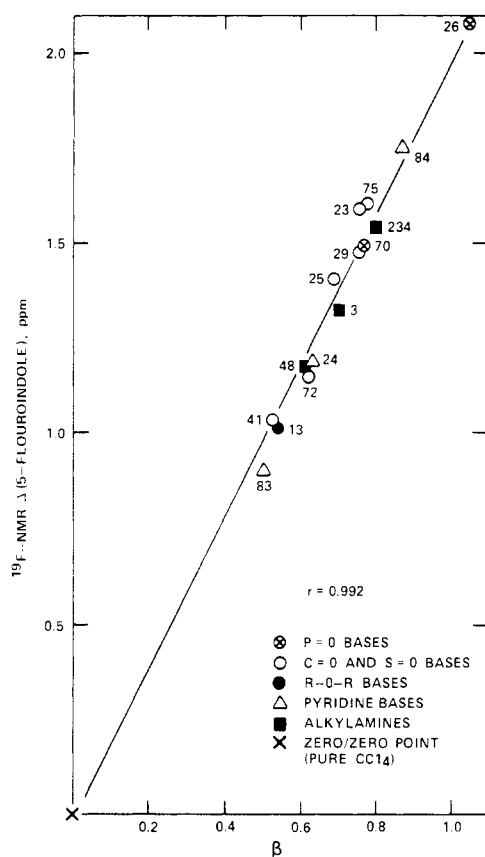


Figure 1. <sup>19</sup>F-NMR  $\Delta$  of 5-fluoroindole plotted against  $\beta$ . Numbering of the data points is as in ref 1 and 10 and Tables I-III.

of Tables I-III) and Gutmann's "donicity numbers (DN)" based on enthalpies of formation of complexes of the HBA bases with antimony pentachloride.<sup>11a,34</sup> Generally, types of properties which are nonlinear with  $\beta$  are nonlinear with one another; see, for example,  $\Delta\nu(C-I)$  of cyanogen iodide vs.  $\Delta\nu(O-H)$  of phenol, reported by Laurence and co-workers.<sup>22a</sup> This does not necessarily apply to the same type property of different indicators, however; Koppel and Paju<sup>35</sup> have demonstrated seemingly good linearity ( $r > 0.975$ ) of  $\Delta\nu(X-H)$  results for 12 HBD acids with up to 89 HBA bases.

Enthalpies of formation of complexes of 4-fluorophenol (4-FP) with HBA bases, reported by Arnett, Mitchell, and

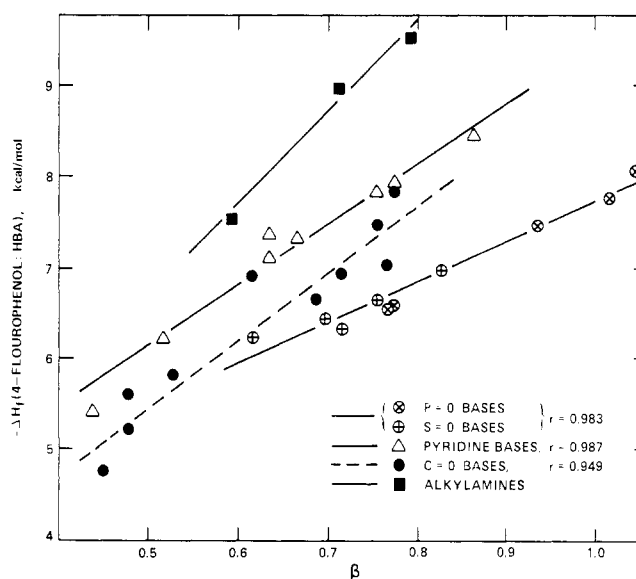


Figure 2. Enthalpies of formation of complexes of 4-fluorophenol with HBA bases plotted against  $\beta$  values of the bases.

Murty,<sup>36</sup> provide a further example of an FD-type correlation. These workers have pointed out that  $\Delta H_f$  and  $\Delta G_f$  of 4-fluorophenol are "correlated by a series of crudely parallel lines, each of about unit slope, correlating free energy with enthalpy for the pyridines, sulfoxides, phosphoroxy compounds, and amides". Since  $\log K (=pK_{HB})$  and hence  $\Delta G_f(4-FP:HBA)$  are linear with  $\beta$ ,<sup>36</sup> it necessarily follows that  $\Delta H_f(4-FP:HBA)$  should show FD-type behavior with  $\beta$ .

A plot of the data is shown in Figure 2, where the non-linearity between the different types of HBA bases is clearly evident. Correlation equations for the individual families are as follows: for P=O and S=O bases, eq 16a, with  $n = 10$ ,  $r = 0.983$ , and  $sd = 0.12$  kcal/mol

$$-\Delta H_f(4-FP:HBA) = 3.16 + 4.49\beta \text{ kcal/mol} \quad (16a)$$

for complexes with C=O bases, eq 16b, with  $n = 10$ ,  $r = 0.949$ , and  $sd = 0.34$

$$-\Delta H_f = 1.86 + 7.21\beta \text{ kcal/mol} \quad (16b)$$

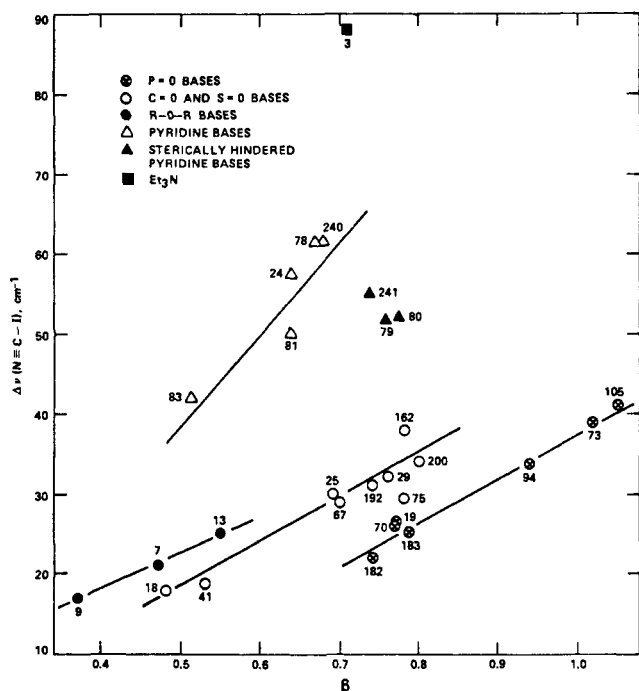
for complexes with pyridine bases, eq 16c, with  $n = 8$ ,  $r = 0.987$ , and  $sd = 0.17$

$$-\Delta H_f = 2.85 + 6.54\beta \text{ kcal/mol} \quad (16c)$$

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(35) Koppel, I. A.; Paju, A. I. *Org. React. (Tartu)* 1974, 11, 121.

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**Figure 3.** Values of  $\Delta\nu(\text{C-I})$  of cyanogen iodide complexes with HBA bases plotted against  $\beta$  values of the bases. Base numbering is as in Tables I-III and ref 1.

The same workers also showed that the data also separate into families in a plot of  $\Delta H_f$  vs.  $\Delta\nu(\text{O-H})$  of 4-fluorophenol.

On the basis of data reported by Laurence and co-workers,<sup>22a</sup>  $\Delta\nu(\text{C-I})$  of cyanogen iodide-HBA complexes also shows FD-type behavior with  $\beta$ . A plot is shown in Figure 3, where it is seen that, as might be expected of

complexation by an iodine atom, steric effects seem to be quite severe. Laurence and co-workers have also shown FD-type behavior in a plot of  $\Delta\nu(\text{C-I})$  against  $\Delta\nu(\text{O-H})$  of phenol.

In a future paper we will show that, when used in combination with the  $\beta$  parameter, a new coordinate covalency parameter,  $\xi$ , allows quantitative intercomparisons between FD and FI behavior patterns through equations of the form of eq 17. Values of  $\xi$  are 0.0 for double bonded

$$\text{XYZ} = \text{XYZ}_0 + b\beta + e\xi \quad (17)$$

oxygen bases, 0.2 for single bonded oxygen bases, 0.6 for pyridine bases, and 1.0 for  $\text{sp}^3$ -hybridized amine bases. Representative  $e/b$  values in eq 17 (which are measures of separations between families in plots like Figures 2 and 3) are  $0.00 \pm 0.05$  for most FI properties, 0.24 for  $\Delta H_f(4\text{-FP:HBA})$ , 0.61 for  $\Delta\nu(\text{O-H})$  of phenol, and 0.79 for  $\Delta\nu(\text{C-I})$  of cyanogen iodide.

In the initial formulation of the  $\beta$  scale,<sup>8a</sup> as in the present study, we obtained  $\beta$  values by averaging  $\beta_i$ 's for the HBA bases acting as both solvents and solutes in nonhydrogen bonding solvents. We wish now, in conclusion, to reemphasize that, except in the base of self-associating amphiprotic compounds (whose apparent  $\beta$  values are very concentration dependent), no statistical distinction between the two types of measurements was evident when appropriate corrections were made for dipolarity/polarizability effects of the neat solvents and dipole/dipole interaction effects of the solutes.

**Acknowledgment.** The work by T.G. was done while on sabbatical at UCI. The work by R.W.T. was supported in part by a grant from the Public Health Service. The work by M.J.K. was done under Naval Surface Weapons Center Foundational Research Task IR-210.

## Butadiynyl-Substituted Vinyl Cations

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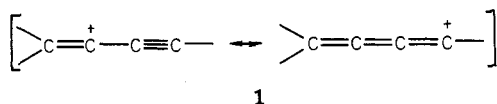
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Received July 1, 1982

The solvolytic reactivity of various 1-(butadiynyl)vinyl triflates,  $\text{R}_2\text{C}=\text{C}(\text{OTf})(\text{C}\equiv\text{C})_2\text{R}'$ , was investigated in aqueous ethanol and 2,2,2-trifluoroethanol (TFE). Activation parameters, solvent  $m$  values, and deuterium isotope effects were determined for these compounds and compared with corresponding parameters for 1-ethynylvinyl triflates,  $\text{R}_2\text{C}=\text{C}(\text{OTf})\text{C}\equiv\text{CR}'$ . For  $\text{R} = \text{CH}_3$  and  $\text{R}' = \text{H}$ , the diyne ester solvolyses in 50% EtOH at 25 °C are 23.5 times faster than those for the alkynyl ester, and both compounds show almost the same isotope effects of 1.05 and 0.94 in 60% EtOH and 97% TFE, respectively. These data are consistent with a unimolecular solvolysis mechanism involving an extended vinyl cation intermediate. The transmission of substituent effects through the diyne group is discussed.

Considerable interest has been evoked recently in the stability, structure, and nature of the reactivity of alkynylvinyl cations such as 1. Recent theoretical studies<sup>1</sup>



indicate that  $\alpha$ -alkynyl substitution destabilizes a vinyl cation in a manner comparable to that observed and predicted for saturated cations. Such calculations are borne out by rate measurements on the solvolysis of a number of alkynylvinyl triflates, 2-5, reported earlier by us<sup>2</sup> and others.<sup>3-5</sup>

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