Linear Solvation Energy Relationships. Part 32.† A Co-ordinate Covalency Parameter, ξ, which, in Combination with the Hydrogen Bond Acceptor Basicity Parameter, β, permits Correlation of Many Properties of Neutral Oxygen and Nitrogen Bases (including Aqueous pK_a)

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Family-dependent (FD) basicity properties are defined as those which have a linear relationship with the hydrogen bond acceptor (HBA) basicity parameter, β, only when families of bases having similar HBA sites are considered separately. Family-independent (FI) properties are those which have a linear relationship with β when all bases are considered together. FD properties can be correlated and meaningfully related to FI properties if, in addition to the β parameter, an empirical co-ordinate covalency parameter, ξ, is used in equations of the form, $XYZ = XYZ_0 + b\beta + e\xi$. Values of ξ are −0.20 for P=O bases, 0.00 for C=O and S=O bases, 0.20 for single-bonded oxygen bases, 0.60 for pyridine bases, and 1.00 for sp^3-hybridized amine bases. By means of the above equation proton transfer basicities (pK_a) are for the first time related to hydrogen bond basicities in a correlation involving all the above types of bonding sites.

In earlier parts, we have described the formulation of three scales of solvent properties, known collectively as the solvatochromic parameters.[1–3] The π* scale of dipolarity–polarizabilities is a measure of the ability of the medium to stabilize a charge or a dipole by virtue of its dielectric effect. The α scale of solvent HBD (hydrogen bond donor) acidities is an index of a protic solvent's ability to act as a donor in a solvent–solute hydrogen bond. The β scale of HBA (hydrogen bond acceptor) basicity quantifies the solvent's ability to act as an acceptor in a solute-to-solvent hydrogen bond. We have shown[4] that β values of non-self-associating compounds are essentially the same, irrespective of whether they are acting as solvents or as solutes, and on this basis we have determined the β values of a number of solid HBA bases. We have also recently reported that solute β values are the leading terms influencing solubilities of organic non-electrolytes in water,[5] as well as octanol–water partition coefficients of aliphatic and aromatic HBA and weak HBD amphiprotic compounds.[6]

We have described two general types of correlations involving the β parameter: (a) correlations wherein, after making provision for the dipolarity–polarizability effect, if any, the property studied is linear with β for all types of HBA bases considered together; and (b) correlations wherein good linearity between the property and β 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 β are often (but not always) nearly parallel. We refer to linear solvation energy relationships of the first type as 'family independent (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, n.m.r. spectral shifts and coupling constants, and free energy properties (*e.g.*, formation constants) of hydrogen bonded complexes. FI correlations of these types which we have so far reported include (a) bathochromic shifts attributable to hydrogen bonding in the u.v.–visible spectra of a large number of aniline and phenol derivatives;[7–11] (b) logarithms of formation constants of complexes of HBA bases with phenol,[7] 4-fluorophenol,[7] methanol,[12] α-naphthol,[12] and tri-n-butylammonium ion;[2] (c) ^{1}H n.m.r. hydrogen bonding shifts of fluorodinitromethane, 3-methylbut-3-en-1-yne, and chloroform,[13] and ^{19}F n.m.r. shifts of 5-fluoroindole,[13] 4-fluorophenol,[7] and bis-(4-fluorophenyl)-mercury;[14] and (d) $J(^{13}C^1H)$ coupling constants of chloroform,[13] and $J(^{119}Sn,C,^1H)$ coupling constants of some polyalkyltin compounds.[14] The ^{19}F n.m.r. shifts of 5-fluoroindole complexes with HBA bases serve as a good example. A plot of these shifts against the β parameter is shown in Figure 1, where it is seen that the data points for the different types of HBA bases are very nicely collinear, with a correlation coefficient, *r*, of 0.992.

FD correlations which we have reported include: (a) i.r. stretching frequency shifts, Δν(O–H, free minus hydrogen bonded) of phenol, 4-fluorophenol, and methanol complexes of HBA bases,[15] and Δν(C–I) of cyanogen iodide complexes;[16] (b) enthalpies of formation of HBA complexes with iodine,[16] 4-fluorophenol,[16] and $SbCl_5$ [the latter being the basis of Gutmann's 'Solvent Donicity (DN)' scale];[14,17] and (c) free energies of formation of I_2–HBA complexes.[16] In addition, FD behaviour has been observed by Taft and his co-workers[12] in a plot of pK_a *versus* pK_{HB} (the latter being an earlier measure of HBA basicity which is linear with β);[7] by Arnett and his co-workers[18] in a plot of ΔH_f of HBA base complexes with 4-fluorophenol against ΔG_f of the same complexes; by Laurence and his co-workers[19] in a plot of Δν(C–I) of cyanogen iodide complexes against Δν(O–H) of the corresponding phenol complexes; and Gramstad and his co-workers[20] in many plots of Δν(O–H) *versus* ΔH_f, Δν(O–H) *versus* log K_{assn}, Δν(O–H) *versus* n.m.r.-Δ, and ΔH_f *versus* n.m.r.-Δ. Further, Taft *et al.*[12] identified the separations observed by them with electronegativity differences between the acceptor atoms. An example of FD behaviour is shown in Figure 2, where Δν(O–H) of phenol complexes with HBA bases in CCl_4 are plotted against β. It is seen that clearly different regression lines are necessary to accommodate the data for triethylamine, pyridine bases, single-bonded oxygen bases, and double-bonded oxygen bases.

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† Part 31, J.-L. M. Abboud, R. W. Taft, and M. J. Kamlet, *J. Chem. Soc., Perkin Trans. 2*, 1985, 815.

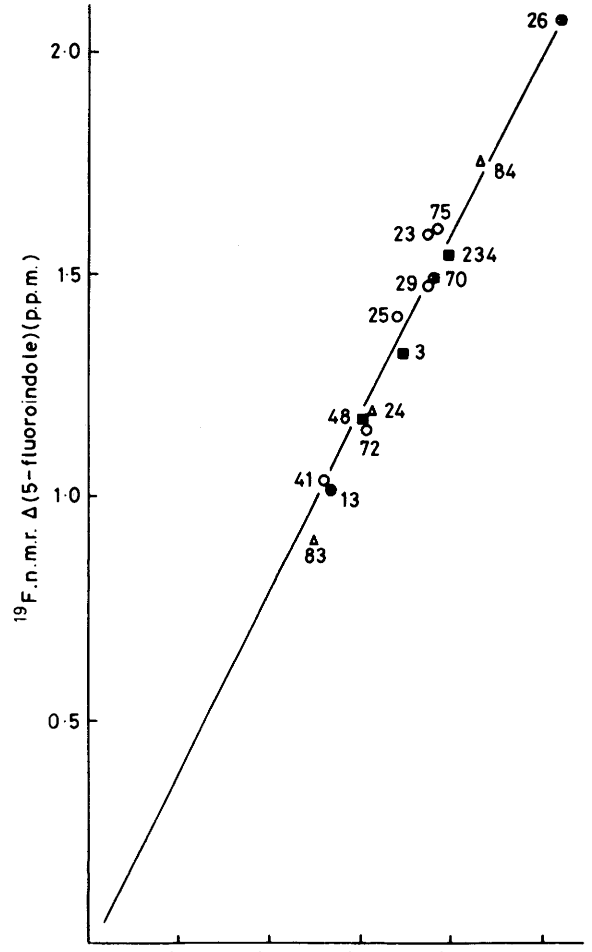

Figure 1. 19F N.m.r. shifts of 5-fluoroindole plotted against β. Numbering of data points is as in Table 1. ×, P=O bases; ○, C=O and S=O; ●, R–O–R bases; △, pyridine bases; ■, alkylamine. The origin represents pure CCl_4. r = 0.992

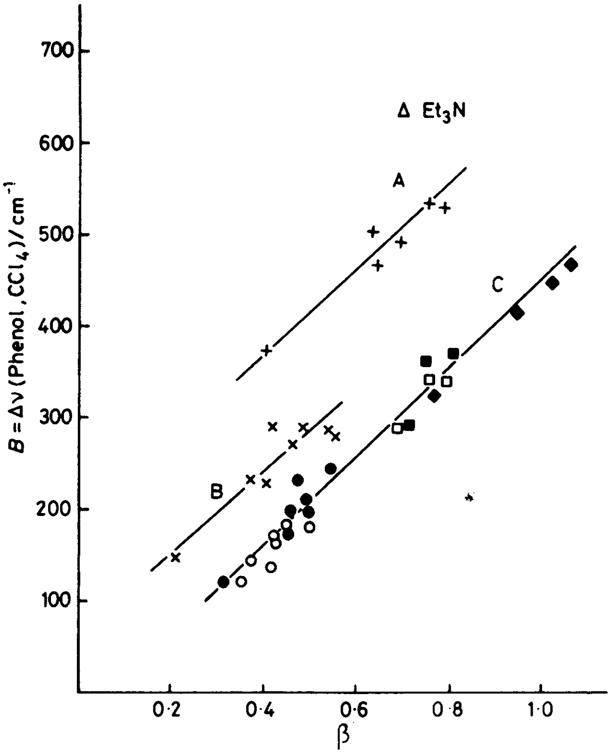

Figure 2. Δν(O–H, free minus hydrogen bonded) of phenol–HBA complexes plotted against β. A, Pyridines; B, single-bonded oxygen bases; C, double-bonded oxygen bases. ○, Esters; ●, aldehydes; ketones; □, amides; ◆, P=O compounds; ×, ethers; +, pyridines; △, triethylamine

A Co-ordinate Covalency Parameter, ξ.—We now report that FD properties can be related meaningfully to FI properties if, in addition to the β parameter, an empirical co-ordinate covalency parameter, ξ, is used in the dual-parameter equation (1). The ξ

$$XYZ = XYZ_0 + b\beta + e\xi \qquad (1)$$

scale has been formulated in the following manner from FD correlations such as that in Figure 2. From equations reported earlier[15] for the regression lines in Figure 2, the Δν(O–H) values for the various classes of bases at β = 0.71 (the β value for the single trialkylamine data point) and the corresponding spacings between the regression lines are as follows:

	Δν(O–H)/ cm^{-1}	Difference/ cm^{-1}
Double-bonded oxygen bases	309	
Single-bonded oxygen bases	377	68
Pyridine bases	516	139
sp^3-Hybridized amine bases	650	134

The spacings between the regression lines are very nearly in the ratio 1.0:2.0:2.0, and on this basis we concluded that the ξ values in equation (1) for the above basicity classes should be in the ratio 0.0:1.0:3.0:5.0. In order to correspond with approximately the same scaling as is used for the π*, α, and β parameters (which makes easier the evaluation of the relative contributions of the various terms to the *XYZ* studied), and to accommodate also some differences between C=O, S=O, and P=O bases which we have seen in other correlations, we have therefore settled on the following ξ values for the various families of bases:

Family	Co-ordinate covalency parameter ξ	q_{H+}, a measure of relative electro-negativity[21,22]
P=O bases	−0.20	
C=O and S=O bases	0.00	0.62 ($CH_2{=}OH^+$)
Single-bonded oxygen bases	0.20	0.57 (H_3O^+)
Pyridine bases	0.60	0.55 ($C_5H_5NH^+$)
sp^3-Hybridized amine bases	1.00	0.47 (NH_3^+)

The choice of zero for the C=O and S=O bases does not imply a nil contribution of the ξ parameter, but rather indicates that the C=O and S=O bases serve as the arbitrary baseline against which the ξ behaviour of the other families is measured.†

Relationship of ξ *to Electronegativity of the Acceptor Atom.*—The values of ξ reported above are interpreted to be approximate measures of the relative co-ordinate covalencies of the bonds which are formed at the base centres. Co-ordinate covalencies of adducts of a given acid decrease in strength (ξ decreases) as the electronegativity of the base centre increases.

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† Hence, for example, correlations of ΔH_f with β and ξ should not have zero intercepts, but rather intercepts which reflect the contribution of the ξ parameter to enthalpies of formation of C=O bases.

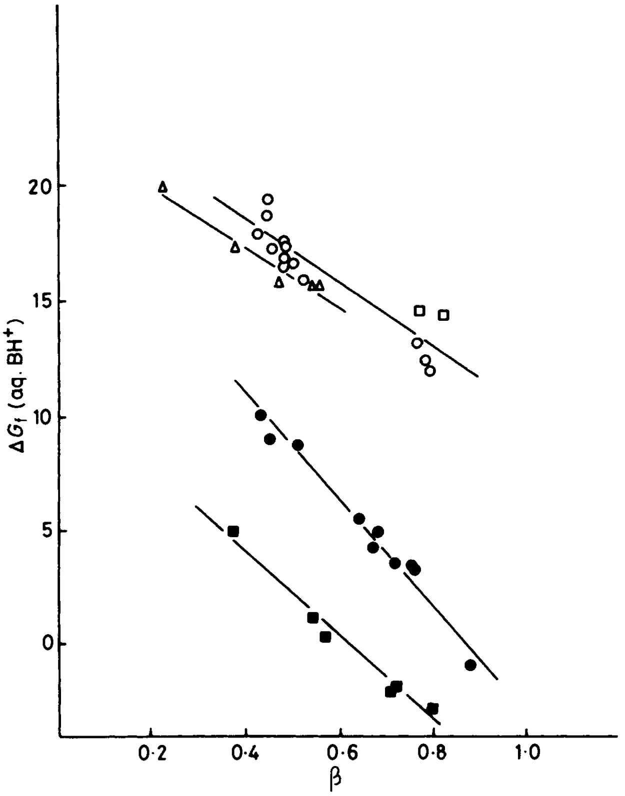

Figure 3. ΔG_f(aq. BH^+) plotted against β. ○, C=O bases; □, S=O bases; △, single-bonded oxygen bases; ●, pyridine bases; ■, amine bases

This follows from the increasingly unfavourable result of placing the positive charge created by co-ordinate covalency on an increasingly electronegative atom. On the other hand, electrostatic bonding of the adducts increases in strength (β increases) as the field intensities of the electron pairs of the base centres are increased by both increasing electronegativity of the acceptor atom, and electron donation by substituent groups in the base.

Ab initio (6-31G* basis) calculations of the charge on hydrogen in HX molecules have recently been shown to measure the relative electronegativities of the substituents, X.[21] Using this approach, the charges of the proton in its adducts with NH_3, C_5H_5N, H_2O, and $CH_2=O$ provide a measure of the relative electronegativities of the family base centres. As is shown above,[22] the electronegativity is in exactly the reverse order of the co-ordinate covalency parameters.

Correlations of Family-dependent Properties with β *and* ξ.—We have found that many disparate types of properties of nitrogen and oxygen bases are well correlated by means of equation (1) and the β and ξ parameters. These include free energy and enthalpy properties of protic and nonprotic Lewis acid–base complexes involving proton transfer as well as hydrogen bonding. Thus, the dual parameter correlation of the phenol Δν results plotted in Figure 2 (data in Table 1) leads to equation (2).

$$\Delta\nu(\text{O–H}) = -34.5 + 512\beta + 313\xi \text{ cm}^{-1} \quad (2)$$
$$n = 43,\ r = 0.989,\ e/b\ [\text{equation (1)}] = 0.616$$

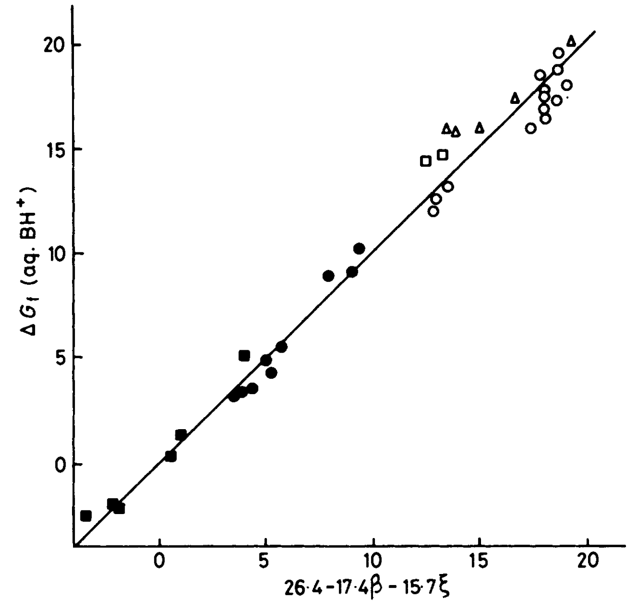

Figure 4. ΔG_f(aq. BH^+) as a function of a linear combination of β and ξ. ○, C=O bases; □, S=O bases; △, single-bonded oxygen bases; ●, pyridine bases; ■, amine bases. $r = 0.993$

As a further important example, free energies of proton transfer to the aqueous base, B, from aqueous NH_4^+, ΔG_f(aq. BH^+), are plotted against β in Figure 3 (data[23] in Table 1). The single-parameter correlation equations for the various families are as in equation (3). The dual-parameter correlation of

Double-bonded oxygen bases

$$\Delta G_f(\text{aq. BH}^+) = 24.2 - 14.0\beta \text{ kcal mol}^{-1} \quad (3a)$$
$$n = 15,\ r = 0.920$$

Single-bonded oxygen bases

$$\Delta G_f(\text{aq. BH}^+) = 22.5 - 12.9\beta \text{ kcal mol}^{-1} \quad (3b)$$
$$n = 5,\ r = 0.970$$

Pyridine bases

$$\Delta G_f(\text{aq. BH}^+) = 18.9 - 20.9\beta \text{ kcal mol}^{-1} \quad (3c)$$
$$n = 9,^\dagger\ r = 0.992$$

sp^3-Hybridized amine bases

$$\Delta G_f(\text{aq. BH}^+) = 11.3 - 18.1\beta \text{ kcal mol}^{-1} \quad (3d)$$
$$n = 6,\ r = 0.987$$

$\Delta G_f(BH^+)$ with β and ξ is given by equation (4). A plot of ΔG_f(expt.) *versus* ΔG_f[equation (4)] is shown in Figure 4. We

$$\Delta G_f(\text{BH}^+) = 26.4 - 17.4\beta - 15.7\xi \text{ kcal mol}^{-1} \quad (4)$$
$$n = 35,^\dagger\ r = 0.992,\ e/b = 0.902$$

believe this to be the first instance wherein hydrogen bonding basicities and proton-transfer basicities involving all the above classes of bases have been quantitatively related to one another within the framework of the same calculation method.

This is particularly important because, as we shall show in future papers, both proton-transfer basicity and hydrogen bond acceptor basicity play important roles in biological systems, and it is often necessary to distinguish between the phenomenology attributable to both types of interactions. Fortunately, the large

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† Excluding 4-dimethylaminopyridine for reasons discussed below. If this result is included the r values become 0.987 and 0.989 for equations (3c) and (4).

Table 1. Data used in correlation of family-dependent physiochemical properties of HBA bases with β and ξ

			Properties correlated[a]														
No.	P=O bases, $\xi = -0.20$	β	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
19	Triethyl phosphate	0.77	331			26					6.59	6.5					
26	Hexamethylphosphoramide	1.05	471		28.1		234		−2.75		8.73	8.0					7.7
70	Trimethyl phosphate	0.77			20.3	26					6.44	6.5					
68	Triphenylphosphine oxide	0.94	420			34						7.7		−0.20			
73	Trimethylphosphine oxide	1.02	450			39						7.4					
180	Triphenyl phosphate	0.62										6.7					
182	$CHCl_2P(O)(OEt)_2$	0.74				22											
183	$CH_2ClP(O)(OEt)_2$	0.79				25											
	C=O, S=O, and N=O bases, $\xi = 0.00$																
11	Ethyl acetate	0.45	181	17.3	18.1		91	3.0	0.04	4.8	4.74		2.43				4.4
16	Butan-2-one	0.48	209	16.9			109	3.35	−0.02		5.20		3.05				
18	Acetone	0.48	224	16.5	18.2	18	123	3.65	−0.07	5.1	5.59						5.0
23	Dimethylacetamide	0.76	343	13.2	26.8		178	5.15	−1.60	6.8	7.44	6.6	4.43	−0.59			6.4
25	Dimethylformamide	0.69	291		26.4	30	166	5.0	−1.10	6.1	6.97		4.14	−0.98	5.5	5.21	6.1
27	Butyrolactone	0.49	190		18.0		118										
28	*N*-Methylpyrrolidone	0.77	330		27.0				−1.65		7.38	7.0					
29	Dimethyl sulphoxide	0.76	362	14.7	25.2	32	192		−1.70	6.9	7.21	6.6	4.66	−0.68			6.3
38	Ethyl formate	0.36			17.0			2.15	0.42								
39	Ethyl chloroacetate	0.35	125				99	1.95									
41	Cyclohexanone	0.53	242		18.3	19	133				5.68	5.8					
49	Ethyl benzoate	0.41	142					2.4	0.20								
51	Cyclopentanone	0.52		16.0	18.6		124		−0.31		5.50						
52	Methyl acetate	0.42	170	18.0	17.5		88	2.9	0.16								
53	Acetophenone	0.49	202	18.5	17.8		108	3.2	−0.08								
65	Methyl t-butyl ketone	0.48		17.4	17.4		97		−0.08								
66	Benzaldehyde	0.44	180	18.8	17.9		105	2.8	0.38								
67	Diphenyl sulphoxide	0.68	294		21.6	29						6.2					
71	2,6-Dimethyl-γ-pyrone	0.79		12.0								6.9			5.5	5.83	
74	Di-n-butyl sulphoxide	0.83	373		25.7							6.9					
75	Tetramethylurea	0.78	340	12.5	26.0	29.5		5.2	−1.58	6.6		7.8			6.4	5.68	
76	Benzophenone	0.44	192	19.4	15.0			2.6	−0.09								
77	Biacetyl	0.31	121														
85	Diethyl carbonate	0.38	145					2.55	0.28		4.20						
140	3-Methylbutan-2-one	0.48		17.5	17.9												
155	Pentan-3-one	0.45			17.3				−0.01								
160	*NN*-Dimethylbenzamide	0.72										6.9					
173	Dimethyl carbonate	0.38			16.2			2.2	0.34								
174	Methyl benzoate	0.39			14.2			2.2	0.29								
193	Phenyl methyl sulphoxide	0.71										6.3					
192	Dibenzyl sulphoxide	0.74				25.5											
200	Tetramethylene sulphoxide	0.80		14.4		34				7.2	7.64						
221	Pyridine *N*-oxide	0.85								7.9		7.5					
	Single-bonded oxygen bases, $\xi = 0.20$																
4	Di-isopropyl ether	0.49	293				124		0.29	6.0							
5	Di-n-butyl ether	0.46	285				129			6.0							5.8
7	Diethyl ether	0.47	280	15.9	18.9	20.5	129	4.2	0.08	6.2	5.57	5.6	2.96				5.1
9	Dioxane	0.37	237	17.3	17.7	17	128		0.25	5.6	5.10		3.11				
13	Tetrahydrofuran	0.55	287	15.8	21.6		145	5.3	−0.54	6.0	5.75	5.6	3.06				
19	Anisole	0.22	155	20.0			75				3.13		1.69				
40	Tetrahydropyran	0.54	290	15.7		25	145			6.1							
46	Dibenzyl ether	0.41	253								4.59						
59	Diphenyl ether	0.13	123								1.89		1.10				
61	1,2-Dimethoxyethane	0.41	238				123				5.75						
86	Di-n-propyl ether	0.46	279				125										
87	Phenetole	0.20	158				77										
	Pyridine bases, $\xi = 0.60$																
24	Pyridine	0.64	472	5.5	30.6	57.5		7.47	−3.03	8.0	7.40	7.10	4.47	0.00	15.4	6.68	7.8
78	4-Methylpyridine	0.67	497	4.4	32.1	61.5		8.93	−3.52		7.59	7.3	4.62	0.64	16.6	6.92	
79	2,6-Dimethylpyridine	0.76	535	3.3								7.8					
80	2,4,6-Trimethylpyridine	0.78	531								7.47	7.9					
81	Quinoline	0.64	494			50		7.22	−2.82			7.35	4.57				
82	3,5-Dichloropyridine	0.42	374														
83	3-Chloro(bromo)pyridine[d]	0.51		8.8	28.4	45.5			−1.86			6.2			11.7	6.18	
84	4-Dimethylaminopyridine	0.87		−0.8	36.2				−5.07					2.48	23.3	7.46	
239	Pyrimidine	0.48			27.0												
240	3-Methylpyridine	0.72		4.9		61.5		7.95	−3.40								

Table 1. (*continued*)

No.		β	Properties correlated[a] 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Pyridine bases, ξ = 0.60 (*continued*)																
241	2,4-Dimethylpyridine	0.74		3.5		55											
242	4-Methoxypyridine	0.72		3.6	32.9												
b	4-Cyanopyridine	0.43[b]		10.1													
b	4-Trifluoromethylpyridine	0.45[b]		9.0													
	Amine bases, ξ = 1.00																
3	Triethylamine	0.71	650	−2.0	35.0[c]	88	314	12.0	−4.95	9.1	8.92		5.53	1.51	24.9	7.26	8.8
48	Tri-n-butylamine	0.62					290		−4.1						25.8	7.36	
49	*NN*-Dimethylbenzylamine	0.57		0.5											21.5	6.96	
225	Triallylamine	0.54		1.3											21.4	6.94	
226	Tri-n-propylamine	0.56							−4.1								
229	2,2,2-Trifluoroethylamine	0.37		5.0													
233	n-Butylamine	0.72		−1.9					−4.2					2.07			
234	Quinuclidine	0.80		−2.6					−7.52	9.0							

[a] Properties correlated are: 1 $\Delta\nu$(O–H) of the phenol complex in CCl_4;[16] 2 aqueous ΔG_f of BH^+;[23] 3 $-\Delta H_f$ of the BF_3 complex in CH_2Cl_2 (present investigation); 4 $\Delta\nu$(C–I) of the ICN complex in CCl_4;[19] 5 $\Delta\nu$(O–D) of the MeOD complex in the pure base solvent;[16] 6 ΔH_f of the I_2 complex in heptane;[19] 7 ΔG_f of the I_2 complex in heptane;[19] 8 $-\Delta H_f$ of the phenol complex in CCl_4 or C_6H_{12};[31] 9 $-\Delta H_f$ of the 4-fluorophenol complex in the pure base solvent;[18] 10 $-\Delta H_f$ of the 4-fluorophenol complex in CCl_4;[18] 11 $-\Delta H_f$ of the n-butanol complex in CCl_4 or C_6H_{12};[31] 12 log k/k_0 for the catalysed n-butylaminolysis of 4-nitrophenyl trifluoroacetate in 1,2-dichloroethane;[32] 13 $-\Delta H_f$ of the $4\text{-}FC_6H_4SO_3^-BH^+$ ion pair in CH_2Cl_2;[33] 14 ^{19}F n.m.r. shift of the above ion pair;[33] 15 $-\Delta H_f$ of the trifluoroethanol complex in CCl_4 or C_6H_{12}.[31] [b] Value of β estimated from pK_{HB}. [c] To minimize steric effect, heat of formation is that of Me_3N complex. [d] 3-Chloro- and 3-bromo-pyridine are assumed to have the same β value.

data base on pK_a values of biologically important molecules can be used with equation (4) to estimate β values of those same molecules.

Additional Correlations of Family-dependent Properties.—We have carried out correlations with β and ξ for 12 additional FD properties. The data used in the correlations and the data sources are assembled in Table 1. The multiple linear regression equations and correlation coefficients are assembled in Table 2, where they are listed in order of increasing e/b values (*i.e.*, increasing separation between families in plots like Figures 2 and 3).

The properties considered include: (a) enthalpies of formation of HBA base complexes with butan-1-ol, 4-fluorophenol, phenol, trifluoroethanol, boron trifluoride, and iodine, and the 4-fluorobenzenesulphonic acid–HBA base ion pair; (b) i.r. stretching frequency shifts for the O–D band of MeOD, the O–H band of phenol, and the C–I band of cyanogen iodide; (c) free energies of formation of base complexes with boron trifluoride, and free energies of transfer of a proton to the aqueous base from aqueous ammonium ion (which is linear with pK_a); ^{19}F n.m.r. shifts of the 4-fluorobenzenesulphonic acid–HBA base ion pair; and (e) logarithms of rate constants for the base-catalysed n-butylaminolysis of 4-nitrophenyl trifluoroacetate. It is seen that they are all well correlated by β/ξ.

Further, we have earlier shown[24] that the formation constants (or ΔG_f values) of complexes of HBA bases with the weak HBD acids diphenylamine, 5-fluoroindole, and chloroform show stronger dependences on the dipole moments of the bases (or their π^* parameters) than on their β-parameters. This result implies a higher degree of electrostatic relative to co-ordinate covalent bonding for the molecular complexes of these bases than for the corresponding molecular complexes of phenol or 4-fluorophenol. Indeed, analysis of the available formation constants[24] of the former acids by equation (1) is consistent with the earlier conclusion. As is shown below, correlation of the data by equation (1) gives in every case negative values of e/b. The r' values in parentheses are the earlier correlations with β and dipole moments or π^*.

$$\log K_f(\text{5-fluoroindole/HBA, CCl}_4) = -1.05 + 3.19\beta - 0.63\xi \quad (5)$$

$$n = 9,\ r = 0.981\ (r' = 0.994),\ e/b = -0.20$$

$$\log K_f(\text{CHCl}_3\text{/HBA, C}_6\text{H}_{12}) = -1.39 + 2.29\beta - 0.74\xi \quad (6)$$

$$n = 11,\ r = 0.972\ (r' = 0.995),\ e/b = -0.32$$

$$\log K_f(\text{Ph}_2\text{NH/HBA, CCl}_4) = -1.25 + 2.78\beta - 1.25\xi \quad (7)$$

$$n = 10,\ r = 0.943\ (r' = 0.985),\ e/b = -0.45$$

As is shown in Table 2 and equations (5)—(7), the above examples cover an e/b [equation (1)] range from −0.45 to +0.90, which means that many of these FD properties would show separate linear regressions for the different families, not only in their correlations with β or with FI properties, but also in their correlations with one another. As an example, Laurence and his co-workers[19] have reported separate regression lines for oxygen, nitrogen, and sulphur bases in a plot of $\Delta\nu$(C–I) of cyanogen iodide complexes with HBA bases (e/b 0.787) against $\Delta\nu$(O–H) of the corresponding phenol complexes (e/b 0.611). (The overall r value for the correlation if all bases had been considered together would be 0.79.) They interpreted the separate regression lines as being due to the fact that $\Delta\nu$(C–I) is a quintessential measure of 'soft basicity', and $\Delta\nu$(O–H) a measure of 'hard basicity'. That $\Delta\nu$(C–I) was approximately linear (r 0.95) with ΔH_f of the corresponding I_2–HBA complexes (e/b 0.828), they attributed to the fact that both indicators were 'soft electron acceptors'. Our interpretation, of course, would be that properties which have similar combinations of co-ordinate covalency and electrostatic bonding, as measured by similar e/b ratios in equation (1), are linear with one another, and properties which have different e/b ratios are non-linear. Such an interpretation would lay to rest most of the controversy surrounding the Badger–Bauer relationship.

Scope and Limitations of the β/ξ Correlations.—In addition to the above examples, an examination of the available (rather

Table 2. Correlations of family-dependent properties by the equation $XYZ = XYZ_0 + b\beta + e\xi$

No.	Property XYZ	XYZ_0 (±)	b (±)	e (±)	n	r (s.d.)	e/b[f]
1	$-\Delta H_f$, Bu^{n}OH–HBA complex in CCl_4 or C_6H_{12}	0.20 (0.21)	5.60 (0.38)	1.26 (0.24)	14	0.982 (0.26)	0.255
2	$-\Delta H_f$, 4-FC_6H_4OH–HBA complex in pure base	1.66 (0.25)	7.20 (0.39)	1.76 (0.25)	23[a]	0.974[a] (0.35)	0.244
3	$-\Delta H_f$, 4-FC_6H_4OH–HBA complex in CCl_4	2.70 (0.29)	5.34 (0.38)	1.67 (0.18)	23[b]	0.955[b] (0.22)	0.313
4	$-\Delta H_f$, PhOH–HBA complex in CCl_4 or C_6H_{12}	2.93 (0.35)	5.13 (0.56)	2.28 (0.26)	17	0.967 (0.34)	0.444
5	log k/k_0, catalysed n-butylaminolysis of 4-$NO_2C_6H_4O$–CO–CF_3 in $ClCH_2CH_2Cl$	−5.04 (0.88)	5.79 (1.12)	2.68 (0.21)	8[c]	0.985[c] (0.22)	0.460
6	$-\Delta H_f$, CF_3CH_2OH–HBA complex in CCl_4 or C_6H_{12}	2.12 (0.36)	5.74 (0.52)	2.81 (0.28)	10	0.982 (0.30)	0.490
7	$\Delta\nu$(O–D), MeOD–HBA complex in pure base	−5.5 (5.7)	239 (11)	145 (7)	27	0.989 (9.1)	0.606
8	ΔG_f, I_2–HBA complex in heptane	2.73 (0.20)	−5.73 (0.36)	−3.27 (0.16)	33[d]	0.982[d] (0.33)	0.570
9	$-\Delta H_f$, BF_3–HBA complex in CH_2Cl_2	6.32 (0.38)	24.4 (1.36)	13.9 (0.82)	34	0.978 (1.33)	0.570
10	$\Delta\nu$(O–H) PhOH–HBA complex in CCl_4	−34.5 (8.9)	512 (14)	313 (12)	43	0.989 (19.6)	0.611
11	^{19}F n.m.r Δ, 4-$FC_6H_4SO_3^-BH^+$ ion pair in CH_2Cl_2	3.06 (0.54)	3.46 (0.70)	2.06 (0.54)	11	0.968 (0.21)	0.673
12	$-\Delta H_f$, 4-$FC_6H_4SO_3^-BH^+$ ion pair in CH_2Cl_2	−15.8 (3.2)	28.9 (4.2)	21.8 (1.1)	11	0.990 (1.24)	0.754
13	$\Delta\nu$(C–I) ICN–HBA complex in CCl_4	−18.5 (3.2)	67.4 (5.0)	53.6 (2.1)	24	0.984 (3.3)	0.795
14	$-\Delta H_f$, I_2–HBA complex in heptane	−0.48 (9.39)	7.48 (0.80)	6.28 (0.38)	23	0.988 (0.43)	0.840
15	ΔG_f(aq. BH^+) in water	26.4 (0.6)	−17.4 (1.1)	−15.7 (4.4)	35[e]	0.992[e] (0.0)	0.902

[a] From diphenyl ether and 1,2-dimethoxyethane; if these are included, $r = 0.969$. [b] From triphenyl phosphate and tetramethylurea; if included, $r = 0.885$. [c] From 4-dimethylaminopyridine; if included, $r = 0.973$. [d] From 4-dimethylaminopyridine and quinuclidine, if included, $r = 0.971$. [e] From 4-dimethylaminopyridine; if included, $r = 0.989$. [f] The degree of collinearity of β with ξ varies with the data set. The highest r value for the covariance is 0.532; the usual r values are below 0.300.

imprecise) values of ΔS_f° for 1:1 complex formation between 4-fluorophenol and HBA bases (usually in dilute CCl_4 solution)[18] indicates that the approximate equation (8) applies. The high

$$-\Delta S_f^\circ = 10(\pm 1) + 3(\pm 1)\beta + 7(\pm 1)\xi \qquad (8)$$

dependency of ΔS_f° on co-ordinate covalency (e/b = *ca.* 2) suggests that internal motions (vibrations, librations) in weak molecular complexes stiffen particularly as co-ordinate covalency is increased for a family of base centres.

Values of e/b in Table 2 and equations (5)—(8) tend to increase (*i.e.*, there are greater separations between families in plots like Figures 2 and 3) with increasing sensitivity of the measured property to greater covalent compared with electrostatic bonding, Thus, for a given acid, e/b tends to increase in the following order of properties: ΔG_f < ^{19}F n.m.r. shift < ΔH_f < $\Delta\nu$ < ΔS_f, and hydrogen bonding < proton transfer. Further, for corresponding properties, e/b ratios appear to increase as follows: hydrogen bonding < nonprotic Lewis acidity (I_2, ICN, BF_3) < proton transfer.

The base properties which conform with equation (1) were measured in solvents which range from hydrocarbon to water. In addition, gas-phase proton and metal-ion affinities are also found to follow equation (1) if allowances are made for enhanced substituent polarizability and resonance effects with the increased electron demands that are involved.[25]

Severe steric effects in acid–base complexing can lead to deviations from equation (1). Thus, in the case of ΔH_f of the BF_3–HBA complexes, the Et_3N value was excluded from the correlation, but not that for Me_3N.* Small steric effects have also been noted in the β values (or antecedent pK_{HB} values),[26] notably for tertiary amines such as Et_3N and $Bu^n{}_3N$. These may give rise to some scatter in either FI or parallel FD behaviour, or oppose other contributing effects (such as variable BH^+ solvation) which would, by themselves, lead to departures from equation (1) in the opposite direction. Aqueous ionic solvation energies of BH^+ are large and variable.[23] However, the relationship between the BH^+ hydration energies and corresponding gas-phase basicities is frequently reciprocal,[27] explaining in part the tendency of ΔG_f(aq. BH^+) to follow equation (1). Substituent polarizability effects are also expected to lead to severe deviations from equation (1).[28]

Stabilization of bases and their conjugate acids by conjugative π-electron donation may vary non-linearly with the difference in electron demand between B and BH^+ or between HBA and HBD:HBA, which is another condition that will lead to deviations from equation (1).[29] For example, omission of the point for 4-dimethylaminopyridine from the series ΔG_f(aq. BH^+), ΔG_f(I_2–HBA), and log k/k_0 (n-butylaminolysis) in Table 2 leads to improved correlations. For these reasons, equation (1) is not expected generally to be a highly precise relationship (although the correlation coefficients in Table 2 for the properties so far studied have been quite respectable). However, with the proper accounting of factors leading to deviations or non-parallel FD behaviour, we believe that equation (1)

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* As another example, we have reported[14] that the Gutmann donicity number, DN, for Et_3N, based on $SbCl_5$–HBA heats of formation, is intermediate between those of pyridine and the oxygen bases. This is because a strong steric effect more than offsets the higher ξ value of Et_3N.

provides a useful quantitative norm for oxygen and nitrogen basicity behaviour of widely differing properties.

In closing, we wish to acknowledge that equation (1) formally and conceptually resembles the Drago E–C treatment,[30,31] with b and β corresponding to E_A and E_B, and e and ξ corresponding to C_A and C_B. However, there are differences, which will be discussed elsewhere in detail.

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