Hydrogen Bonding. Part 10.† A Scale of Solute Hydrogen-bond Basicity using log *K* Values for Complexation in Tetrachloromethane

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A scale of solute hydrogen-bond basicity has been set up using log *K* values for the complexation of a series of bases (*i*) against a number of reference acids in dilute solution in tetrachloromethane, equation (i).

$$\log K^{i} = L_{\mathrm{A}} \log K^{\mathrm{H}_i}_{\mathrm{B}} + D^{\mathrm{A}} \qquad \text{(i)}$$

Thirty-four such linear equations have been solved to yield L_{A} and D_{A} values that characterise the acids, and $\log K^{\mathrm{H}}_{\mathrm{B}}$ values that characterise the base; all the thirty-four equations intersect at a point where $\log K = -1.1$ with *K* on the molar scale. This primary set of $\log K^{\mathrm{H}}_{\mathrm{B}}$ values involved 215 bases, and through a large number of secondary values we have been able to determine $\log K^{\mathrm{H}}_{\mathrm{B}}$ for some 500 bases, that include nearly all the functional groups encountered in organic chemistry. By making use of the 'magic point,' we have transformed $\log K^{\mathrm{H}}_{\mathrm{B}}$ into an entirely equivalent, but more convenient, scale through equation (ii).

$$\beta_2^{\mathrm{H}} = (\log K^{\mathrm{H}}_{\mathrm{B}} + 1.1)/4.636 \qquad \text{(ii)}$$

Since we can take $\beta_2^{\mathrm{H}} = 0$ for all non-basic compounds such as alkanes and cycloalkanes, the new β_2^{H} hydrogen-bond solute basicity scale covers virtually all classes of base.

We show that β_2^{H} is not generally related to measures of full proton-transfer basicity such as aqueous p*K* or gaseous proton affinity (E_{pa}) values, although family dependence is observed, and we stress that solute hydrogen-bond basicity must not be equated with full proton-transfer basicity. We also briefly investigate the solvent dependence of the β_2^{H} values in terms of the Maria–Gal θ-value, and we point out a number of exclusions to the 'reasonably general' β_2^{H} scale.

Because basicity is such a fundamental chemical property, and no doubt also because basicity can be measured relatively easily, a large number of basicity scales are available. Maria and Gal *et al.*[1] have rationalised this area through a principal-components analysis of different basicity scales, or basicity-dependent properties (BDPs). They identified two main components, F_1 and F_2, which can be used to codify BDPs through equation (1); here BDP represents some basicity-dependent property of a series of compounds, *e.g.* log *K* for proton-acceptor equilibria in water, or ΔH° for reaction with boron trifluoride. The components F_1 and F_2 were listed for 22 given bases, and so for any given BDP where sufficient data are available, the constants BDP_0, S_1 and S_2 can be found by multiple linear-regression analysis.[1] Maria and Gal *et al.*[1]

$$\mathrm{BDP} = \mathrm{BDP}_0 + S_1F_1 + S_2F_2 \qquad (1)$$

suggested that F_1 represents a combination of electron delocalisation (or covalent) and electrostatic effects, and that F_2 represents an electrostatic effect. Hence the ratio $S_2:S_1$ will provide a quantitative estimate of the electrostatic:covalent character in the base–acid complex. A more concise description is given by an angle θ defined as $\theta = \tan^{-1}(S_2/S_1)$. Only when S_2/S_1, or θ, is the same for two basicity-dependent properties, $(\mathrm{BDP})^{\mathrm{a}}$ and $(\mathrm{BDP})^{\mathrm{b}}$, will a plot of $(\mathrm{BDP})^{\mathrm{a}}$ against $(\mathrm{BDP})^{\mathrm{b}}$ be linear over all the bases concerned, and hence show family-independent character.

A particular class of BDPs involves hydrogen-bond basicity, which is known to be of crucial importance in numerous physiochemical and biochemical processes,[2–4] and it is our intention to construct a scale of solute hydrogen-bond basicity. We must stress that *solute* hydrogen-bond basicity is distinct from *solvent* hydrogen-bond basicity. Not only will the hydrogen-bond basicity of associated compounds such as alcohols be scaled quite differently for the bulk associated solvent and the monomeric solute, but even for some non-associated compounds there seem to be significant differences between bulk and monomer hydrogen-bond basicities.[5]

Even with the restricted BDP range of solute hydrogen-bond basicity there are still several possibilities for construction of a scale. However, most of the quantities we wished to analyse through such a scale are Gibbs-energy related, *e.g.* partition coefficients of all kinds, as log *P* values. We therefore related our scale to log *K* (or ΔG°) values for 1:1 hydrogen-bond complexation of a series of monomeric bases with various reference acids, in tetrachloromethane at 298 K, so that the thermodynamic basis of the solute hydrogen-bond basicity scale is the same as that of the solute hydrogen-bond acidity scale we

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† Part 9, ref. 4.

Table 1. Calculated values of θ for various reference acids in some non-polar solvents.

Reference acid	Solvent	θ
Diphenylamine	CCl_4	86
4-Bromoaniline	CCl_4	86
N-Methylaniline	C_6H_{12}	*ca.* 85
Trichloromethane	C_6H_{12}	83
Indole	CCl_4	82
t-Butyl alcohol[a]	CCl_4	80
Pyrrole	CCl_4	78
Trichloromethane	CCl_4	78
5-Fluoroindole	CCl_4	77
Methanol	CCl_4	73
TFE	CCl_4	72
Maleimide	CCl_4	70
4-Methoxyphenol	CCl_4	70
4-Fluorophenol	CCl_4	70
Water	CCl_4	69
4-Fluorophenol	C_6H_{12}	69
4-Bromophenol	CCl_4	69
4-Chlorophenol	CCl_4	68
4-Nitrophenol	CH_3CCl_3	68
Phenol	CCl_4	67
4-Iodophenol	CCl_4	67
4-Methylphenol	CCl_4	67
4-Nitrophenol	CCl_4	67
Ethanol	CCl_4	*ca.* 67
Butanol	CCl_4	65
Succinimide	CCl_4	64
HFIP	CCl_4	64

[a] Over a large set of bases, this hydrogen-bonded acid behaves as though it were in the lower set of acids.

have previously set up.[6] Although a number of solute hydrogen-bond basicity scales have been constructed,[7–11] there has been only one attempt to construct a Gibbs energy related scale *i.e.* that of Taft *et al.*,[12] who used log *K* values for the complexation of bases with 4-fluorophenol in tetrachloromethane to set up the pK_{HB} scale. Taft *et al.*[12] showed that the pK_{HB} scale had some generality by the observation that log *K* values for complexation of bases against various alcohols in tetrachloromethane were linear with pK_{HB} (*i.e.* family independent behaviour). However, this was not so for log *K* values for complexation against 5-fluoroindole in tetrachloromethane (*i.e.* family-dependent behaviour),[13] so that the overall generality of the scale was never really established. In the event, little use has been made of the pK_{HB} scale, perhaps because for a scale based on one reference acid only it is not possible to establish a 'zero point,' as we shall see later.

As an essential preliminary, we have analysed[14] data on log *K* values for hydrogen-bond complexation of series of bases against reference acid/solvent systems in terms of the Maria–Gal θ value. A summary of results from ref. 14 is given in Table 1. Even for solute hydrogen-bond basicity in non-polar solvents expressed as Gibbs-energy related quantities, it is not possible to establish a completely general scale, since θ varies by so much that family-dependent behaviour will be observed (as found by Taft *et al.*[13] for the 5-fluoroindole reference acid). We suggested[14] that a set of reference acids in tetrachloromethane for which θ varied between about 64–73° could be used to construct a 'reasonably general' scale. Such a scale will include not only all classes of bases against the reference acids giving rise to $64 < \theta < 73°$, but also 'polar' bases containing CO, SO, and PO functionalities against the other reference acids. In other words, only combinations of bases such as pyridines, other amines, and ethers against reference acid/tetrachloromethane systems with $\theta > 75°$ are excluded.*

Data Analysis

Our analysis closely follows that previously given in the construction of a solute hydrogen-bond acidity scale.[6] We assemble the data as a series of log *K* values for hydrogen-bond complexation of bases with a given reference acid in tetrachloromethane [equation (2)]. We exclude the acid–base combinations mentioned above, and in this primary analysis restrict the reference acids to those for which log *K* values for at least 10 bases are available. Furthermore, we allow bases in this primary analysis only if the log *K* values for a given base against at least two reference acids are known. All the log *K* values refer to dilute solutions in tetrachloromethane with *K* in units of $dm^3\ mol^{-1}$ at 298 K. This produced a data base of 1 040 log *K* values, covering 215 bases in 34 reference acid sets. The log *K* values were taken from the literature references given previously,[6] considerable care being taken in checking the original data. The log *K* values for bases against the 34 reference acids can be assembled as a system of 34 linear equations [(3)], where

$$\mathrm{B} + \mathrm{H{-}A} \overset{\mathrm{CCl_4}}{\rightleftharpoons} \mathrm{B}\cdots\mathrm{H{-}A} \qquad (2)$$

$$\begin{aligned} \log K^i \text{ (bases against acid 1)} &= L_1 \,.\, \log K_B^{H_i} + D_1 \\ \vdots \qquad\qquad & \qquad \vdots \qquad\quad \vdots \qquad\qquad (3) \\ \log K^i \text{ (bases against acid A)} &= L_A \,.\, \log K_B^{H_i} + D_A \end{aligned}$$

L_A and D_A characterise the given reference acid, and log $K_B^{H_i}$ characterises the base. The log K_B^H values thus constitute a scale of hydrogen-bond basicity over all the 34 equations (1 ... A). A computer program was devised to solve the set of equations by an iterative procedure, and we were able to fit the 1 040 log *K* values with a standard deviation, *s*, of 0.078 log units. This must be close to the 'level of exhaustive fit,' which we estimate is *ca.* 0.05–0.10 log units, as judged from various inter-laboratory determinations of log *K* values.

Although this 'unconstrained' set of equations leads to excellent correlations of the experimental log *K* values, we know that a condition for the existence of both an acidity scale and a basicity scale derived from the same log *K* values is that either the lines generated by equation (3) are all parallel or else all intersect at a given 'magic point.' We know also that if the lines do so intersect, then the magic point must be the same for both the acidity and basicity scale. Since we have previously found a magic point of −1.1 log units when constructing our solute acidity scale,[6] we can test the coherence of the entire system of equations by a similar analysis of equation (3). A plot of the overall standard deviation of observed and calculated log *K* values as a function of the selected intersection point is given in the Figure, together with a similar plot found[6] for the equations used to construct the acidity scale. It is clear that the same magic point of −1.1 log units is observed in both cases. For the set of equations (3), the standard deviation found on forcing all 34 equations through this point is 0.081 log units, almost identical with the standard deviation of 0.078 log units for the unconstrained equations. We therefore repeated the solution of the 34 equations (1 ... A) when all 34 were constrained to intersect at a point where log $K = -1.1$; the resulting L_A and D_A values are given in Table 2, together with

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* We have subsequently found that pentachlorophenol/tetrachloromethane gives rise to $\theta = 55 \pm 3°$, and hence exclude these given bases against this reference acid system as well.

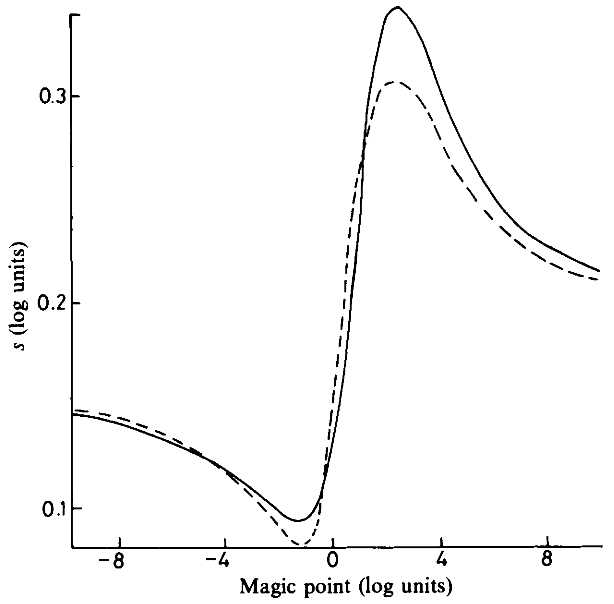

Figure. Plots of the overall standard deviation of observed and calculated log K values as a function of the selected intersection point; – – –, this work; ———, from ref. 6.

Table 2. The reference acids in tetrachloromethane at 298 K used in the set of equations (3).

No.	Reference set	L_A	D_A	s (log K^0)	n_B
1	Phenol	0.946	−0.057	0.088	189
2	4-Fluorophenol	1.000	0.000	0.089	74
3	4-Chlorophenol	1.065	0.074	0.054	38
4	4-Bromophenol	1.075	0.084	0.043	32
5	4-Iodophenol	1.080	0.090	0.048	16
6	4-Nitrophenol	1.299	0.328	0.087	31
7	4-Methylphenol	0.907	−0.101	0.035	31
8	4-(t-Butyl)phenol	0.886	−0.125	0.044	13
9	4-Methoxyphenol	0.911	−0.096	0.039	26
10	3-Chlorophenol	1.102	0.113	0.077	26
11	3-Nitrophenol	1.241	0.269	0.109	19
12	3-Methylphenol	0.909	−0.099	0.052	24
13	2-Methylphenol	0.819	−0.198	0.064	15
14	3,5-Dichlorophenol	1.230	0.254	0.062	27
15	1-Naphthol	0.968	−0.034	0.071	42
16	Water	0.554	−0.490	0.067	13
17	Methanol	0.582	−0.459	0.090	49
18	Ethanol	0.538	−0.507	0.063	20
19	Butanol	0.516	−0.533	0.100	14
20	t-Butyl alcohol	0.496	−0.553	0.072	17
21	TFE	0.910	−0.098	0.063	39
22	HFIP	1.224	0.250	0.121	26
23	Thiocyanic acid	1.185	0.206	0.177	25
24	Maleimide	0.784	−0.236	0.087	11
25	Succinimide	0.771	−0.250	0.165	11
30	Pentachlorophenol	0.892	−0.118	0.077	49
31	Pyrrole	0.643	−0.391	0.077	35
32	Indole	0.712	−0.315	0.074	39
33	5-Fluoroindole	0.744	−0.280	0.052	14
34	4-Bromoaniline	0.489	−0.561	0.083	8
35	Diphenylamine	0.513	−0.535	0.121	22
36	*N*-Methylaniline	0.604	−0.435	0.083	16
39	Trichloromethane	0.326	−0.741	0.036	18
40	Cyanoethyne	0.501	−0.550	0.101	11

the s value for the particular equation, and n_B is the number of bases used to construct that particular equation. Of course, the actual L_A and D_A values can be scaled in any way; we chose $L_A = 1$ and $D_A = 0$ for the set with 4-fluorophenol as the reference acid, see Table 2. The log K_B^H values which generate the equations in Table 2 are given in Table 3, together with the standard deviation of the log K_B^H value, and n, the number of equations in which that particular base appeared. As mentioned above, $n \geqslant 2$ because all bases for which $n = 1$ were removed. We regard the log K_B^H values collected in Table 3 for 215 bases as 'primary' values.

Once the constants L_A and D_A are known for a reference acid, then a very large number of 'secondary' log K_B^H values can be obtained for bases for which a log K value is known only against the one reference acid. A selection of these secondary values for some important bases is given in Table 4.

The β_2^H *Scale of Solute Hydrogen-bond Basicity.*—The log K_B^H values shown in Tables 3 and 4 represent a reasonably general scale of solute hydrogen-bond basicity, thermodynamically related to Gibbs energies of hydrogen-bond complexation. For many purposes it is convenient (or even essential) to construct a basicity scale with a given 'zero point,' *i.e.* a point on the scale that corresponds to zero hydrogen-bond basicity so that compounds such as alkanes and cycloalkanes can be included in the scale. If a Gibbs-energy related scale is tied to one reference acid only (as is the case with the pK_{HB} scale), it is not possible to deduce the 'zero point.' As mentioned above, this is perhaps one reason why the pK_{HB} scale has been very little used. However, our method of analysis, using a large number of reference acids, has provided an automatic zero point—namely the magic point of −1.1 log units. At this point, all bases appear equally weak because we have reached the lower limit of hydrogen bonding as a significant contributor to molecular association. We can either use the log K_B^H scale as such, and define log $K_B^H = -1.1$ for all non-hydrogen-bonding bases, or, more conveniently, we can simply shift the zero point to 0.0 by addition of 1.1 units to all the log K_B^H values. It is rather convenient, at the same time, to compress the scale somewhat, so that β_2^H for the base hexamethylphosphoric triamide (HMPT) is unity. The conversion from log K_B^H to β_2^H then becomes equation (4) which is the defining equation for the β_2^H scale of solute hydrogen-bond basicity.

$$\beta_2^H = (\log K_B^H + 1.1)/4.636 \qquad (4)$$

All the log K_B^H values in Tables 3 and 4 can be converted into β_2^H values *via* equation (4), but in addition we can take β_2^H as zero for all alkanes, cycloalkanes, rare gases, and a number of other non-basic solutes. A rather large number of β_2^H values can also be estimated in various ways. For example we have observed that β_2^H is constant to within any reasonable experimental error* along an homologous series (with the occasional exception of the first member of the series), as can be seen from the data presented in Table 5. In addition, the effect of chain-branching on β_2^H is remarkably small, there being very little change in β_2^H even on replacing a methyl by a t-butyl group, see Table 6. Only in one case, that of di(t-butyl) ether, can any lowering of β_2^H by a steric effect be detected, whilst any inductive or polar effects of branched-chain alkyl groups seem to be too small to be observed. We can, therefore, assign with some confidence 'average' β_2^H values to various alkyl-substituted compounds. This cannot be done with halogen or other substituents, as can be seen from Table 7, where halogen substituents markedly lower β_2^H.

In the aromatic series, 2-methylaniline is slightly less basic than expected, see Table 8, and it is probable that 2,6-alkyl-substituted anilines will be appreciably less basic than aniline.

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* Since log K_B^H for primary bases is subject to $s = 0.081$ log units, the corresponding error in β_2^H will be around 0.02 units.

Table 3. Primary values[a] of $\log K^{\mathrm{H}}_{\mathrm{B}}$.

Solute	$\log K^{\mathrm{H}}_{\mathrm{B}}$	$s(\log K^{\mathrm{H}}_{\mathrm{B}})$	*n*
1-Chlorobutane	−0.608	0.411	2
2-Chloro-2-methylpropane	−0.224	0.075	2
1-Bromobutane	−0.166	0.382	2
2-Bromo-2-methylpropane	−0.325	0.266	2
Benzene	−0.422	0.118	12
Toluene	−0.441	0.101	9
o-Xylene	−0.349	0.096	7
m-Xylene	−0.287	0.075	7
p-Xylene	−0.272	0.061	10
Mesitylene	−0.169	0.085	13
1,2,4,5-Tetramethylbenzene	−0.158	0.101	3
Hexamethylbenzene	0.095	0.149	10
Naphthalene	−0.119	0.049	6
Phenanthrene	−0.091	0.063	6
Chlorobenzene	−0.589	0.220	4
Bromobenzene	−0.758	0.200	2
Dimethyl ether	0.907	0.044	2
Diethyl ether	0.988	0.140	14
Dipropyl ether	0.960	0.088	2
Di-isopropyl ether	1.020	0.132	11
Dibutyl ether	0.842	0.151	6
Di(t-butyl) ether	0.639	0.070	3
Ethyl (t-butyl) ether	1.196	0.074	2
Trimethylene oxide (oxetane)	1.393	0.095	2
Tetrahydrofuran	1.264	0.085	10
1,4-Dioxane	1.101	0.132	12
Tetrahydropyran	1.113	0.140	5
Diphenyl ether	0.029	0.222	3
Dibenzyl ether	0.700	0.039	3
Anisole	0.105	0.066	4
1,8-Cineole	1.280	0.141	4
Benzaldehyde	0.826	0.118	3
Propanone	1.205	0.148	22
Butanone	1.131	0.101	4
Pentan-3-one	0.942	0.239	2
4-Methylpentan-2-one	0.992	0.079	4
Cyclopentanone	1.340	0.233	4
Cyclohexanone	1.325	0.113	15
Mesityl oxide	1.215	0.072	5
Piperitone	1.384	0.073	4
Hexafluoropropanone	−0.195	0.136	2
Acetophenone	1.268	0.262	5
Benzophenone	1.026	0.146	11
2,6-Dimethyl-4-pyrone	2.497	0.095	3
Flavone	1.925	0.059	3
4-Methoxyacetophenone	1.337	0.010	2
Methyl formate	0.655	0.172	4
Methyl acetate	0.746	0.234	5
Ethyl acetate	0.968	0.170	12
Vinyl acetate	0.746	0.169	2
2-Dimethylamino-3,3-dimethylazirine	2.492	0.058	6
Me_2NCN	1.497	0.089	2
Nitrobenzene	0.482	0.259	2
Acetonitrile	0.933	0.150	12
1-Cyanobutane	0.944	0.064	9
Chloroacetonitrile	0.461	0.100	2
Trichloroacetonitrile	−0.323	0.235	2
Benzonitrile	0.860	0.109	4
Phenylacetonitrile	0.783	0.171	2
t-Butylamine	2.203	0.005	2
Diethylamine	2.165	0.096	4
Di-isopropylamine	1.991	0.013	2
Cyclohexyldimethylamine	2.144	0.091	2
Triethylamine	2.001	0.083	15
Tripropylamine	1.605	0.095	3
Tributylamine	1.667	0.081	4
Triallylamine	1.387	0.123	2
Aniline	0.651	0.057	12
Benzylamine	1.796	0.065	2
Dibenzylamine	1.443	0.146	2
Tribenzylamine	0.328	0.204	4
N,*N*-Dimethylbenzylamine	1.661	0.143	2
3-Aminotoluene	0.732	0.056	4
4-Aminotoluene	0.851	0.034	4
N,*N*-Dimethylaniline	0.527	0.110	2
N,*N*-Diethylaniline	0.817	0.475	2
3-Fluoroaniline	0.306	0.143	3
4-Fluoroaniline	0.579	0.083	4
3-Chloroaniline	0.234	0.006	2
4-Chloroaniline	0.469	0.101	4
3-Bromoaniline	0.169	0.068	3
4-Bromoaniline	0.457	0.107	4
3-Iodoaniline	0.233	0.108	3
4-Iodoaniline	0.348	0.112	3
3-Methoxyaniline	0.741	0.016	3
4-Methoxyaniline	1.006	0.011	4
N,*N*-Dimethylformamide	1.973	0.076	19
N,*N*-Diethylformamide	2.015	0.055	2
N-Methylacetamide	2.217	0.054	2
N,*N*-Dimethylacetamide	2.283	0.091	21
N,*N*-Diethylacetamide	2.283	0.131	8
N,*N*-Dicyclohexylacetamide	2.452	0.173	2
N-Acetylpiperidine	2.297	0.053	3
N,*N*-Dimethylpropanamide	2.182	0.032	2
N,*N*-Diethylpropanamide	2.093	0.149	6
N,*N*-Dicyclohexylpropanamide	2.215	0.124	2
N-Propionylpiperidine	2.224	0.058	2
N,*N*-Diethylbutanamide	2.163	0.043	2
N-Butyrylpiperidine	2.209	0.007	2
Tetramethylurea	2.346	0.042	13
1,1,1-Trifluoro-*N*,*N*-dimethylacetamide	1.011	0.105	3
1-Chloro-*N*,*N*-dimethylacetamide	1.737	0.061	3
1-Chloro-*N*,*N*-diethylacetamide	1.780	0.067	7
1,1-Dichloro-*N*,*N*-diethylacetamide	1.398	0.134	2
1-Chloro-*N*,*N*-dicyclohexylacetamide	1.727	0.026	2
N-Chloroacetylpiperidine	1.765	0.012	2
N,*N*-Diphenylacetamide	1.874	0.019	6
N,*N*-Diphenylpropanamide	1.750	0.024	2
N,*N*-Diphenylbutanamide	1.807	0.014	2
N,*N*-Diphenylchloroacetamide	1.404	0.011	2
N,*N*-Dimethylbenzamide	2.025	0.243	3
N,*N*-Diethylbenzamide	2.147	0.102	3
N,*N*-Dicyclohexylbenzamide	2.231	0.151	2
N-Benzoylpiperidine	2.164	0.074	2
N,*N*-Diphenylbenzamide	1.685	0.064	2
N-(4-Nitrobenzyl)piperidine	1.726	0.014	2
N,*N*-Diethyl-4-nitrobenzamide	1.747	0.002	2
N,*N*-Dicyclohexyl-4-nitrobenzamide	1.754	0.064	2
4-Nitro-*N*,*N*-diphenylbenzamide	1.272	0.039	2
Pyridine	1.797	0.153	21
2-Methylpyridine	1.796	0.219	2
3-Methylpyridine	1.776	0.237	2
4-Methylpyridine	1.937	0.172	5
2,4-Dimethylpyridine	1.885	0.306	2
2,6-Dimethylpyridine	1.858	0.285	2
2,4,6-Trimethylpyridine	2.114	0.260	5
2-Ethylpyridine	1.684	0.245	2
2-(t-Butyl)pyridine	1.206	0.199	2
2-Fluoropyridine	0.901	0.037	3
2-Chloropyridine	0.986	0.099	3
3-Chloropyridine	1.161	0.210	2
2-Bromopyridine	0.917	0.033	2
3-Bromopyridine	1.257	0.038	3
4-(*N*,*N*-Dimethylamino)pyridine	2.883	0.104	2
Pyridine *N*-oxide	2.651	0.058	6
N-Methylpyrrolidin-2-one	2.445	0.110	13
N-Phenylpyrrolidin-2-one	1.824	0.048	3
N-Methyl-2-pyridone	2.443	0.056	4
N-Methylimidazole	2.634	0.109	7
2-Aminopyrimidine	1.727	0.040	8
Pyridazine	1.849	0.027	8
Pyrimidine	1.337	0.028	8

Table 3 (*continued*)

Solute	log K_B^H	s (log K_B^H)	n
3-Methyl-4-pyrimidone	1.853	0.049	7
N-Methylmorpholine	1.713	0.058	4
Pyrazine	1.125	0.037	8
1,4-Diazabicyclo[2.2.2]octane	2.638	0.127	4
Nicotine	2.087	0.016	5
3-(*N*,*N*-Diethyl)nicotinamide	2.177	0.046	4
1,3-Dimethyluracil	1.760	0.036	8
Quinoline	1.835	0.021	2
N-(2-Chlorophenyl)pyrrolidin-2-one	2.125	0.084	3
N-(2-Methoxyphenyl)pyrrolidin-2-one	2.279	0.072	3
N-(3-Methylphenyl)pyrrolidin-2-one	1.844	0.053	3
N-(3-Chlorophenyl)pyrrolidin-2-one	1.498	0.109	3
N-(3-Methoxyphenyl)pyrrolidin-2-one	1.794	0.036	3
N-(4-Methylphenyl)pyrrolidin-2-one	1.908	0.066	3
N-(4-Ethylphenyl)pyrrolidin-2-one	1.919	0.073	3
N-(4-Chlorophenyl)pyrrolidin-2-one	1.555	0.084	3
N-(4-Methoxyphenyl)pyrrolidin-2-one	2.005	0.051	3
Diethyl sulphide	0.220	0.092	9
Ethyl methyl sulphide	0.020	0.226	2
Dibutyl sulphide	0.244	0.111	3
Di(t-butyl) sulphide	0.225	0.189	2
Tetrahydrothiophene	0.126	0.072	3
Dimethyl sulphoxide	2.492	0.136	25
Di-isopropyl sulphoxide	2.558	0.170	2
Dibutyl sulphoxide	2.540	0.005	2
Diphenyl sulphoxide	1.990	0.056	14
Di(*p*-tolyl) sulphoxide	2.119	0.007	2
Tetrahydrothiophene *S*-oxide	2.472	0.002	2
Diphenyl sulphone	1.274	0.135	2
Sulpholane	1.324	0.037	3
Diethyl sulphite	0.826	0.120	3
Trimethylphosphine oxide	3.444	0.030	4
Triethylphosphine oxide	3.617	0.108	4
Triphenylphosphine oxide	3.159	0.069	8
Dimethyl phosphite	2.237	0.146	4
Diethyl phosphite	2.342	0.121	4
Di-isopropyl phosphite	2.488	0.160	4
Dimethyl ethylphosphonate	2.658	0.062	3
Diethyl methylphosphonate	2.723	0.071	5
Diethyl ethylphosphonate	2.750	0.065	4
Diethyl isopropylphosphonate	2.717	0.106	2
Di-(1-chloropropyl) methylphosphonate	2.545	0.076	4
Diethyl chloromethylphosphonate	2.426	0.073	4
Diethyl dichloromethylphosphonate	2.150	0.109	4
Diethyl trichloromethylphosphonate	1.893	0.199	5
Trimethyl phosphate	2.431	0.068	8
Triethyl phosphate	2.574	0.108	5
Tributyl phosphate	2.476	0.064	2
Triphenyl phosphate	1.791	0.111	2
Ethyl isothiocyanate	−0.062	0.124	2
Methyl thiocyanate	0.564	0.023	2
Ethyl thiocyanate	0.597	0.031	2
Tetramethylthiourea	1.283	0.072	13
O-Methyl *N*,*N*-dimethylthiocarbamate	0.827	0.093	2
Methyl *N*,*N*-dimethyldithiocarbamate	0.741	0.161	2
N,*N*-Dimethylthioacetamide	1.182	0.093	4
N,*N*-Dimethylthiobenzamide	1.106	0.178	2
N,*N*-Dimethylamino(thioxo)acetonitrile	0.607	0.115	2
N,*N*-Dimethylmethanesulphinamide	2.313	0.075	11
N,*N*-Dimethylbenzenesulphinamide	2.069	0.065	11
N,*N*-Dimethyltoluene-*p*-sulphinamide	2.075	0.112	5
N-Methylmethanesulphonamide	1.256	0.039	7
N,*N*-Dimethylmethanesulphonamide	1.296	0.066	9
N,*N*-Dimethylbenzenesulphonamide	1.357	0.178	5
N,*N*-Dimethyltoluene-*p*-sulphonamide	1.430	0.180	5
Hexamethylphosphoramide	3.536	0.119	21
Diethyl *N*,*N*-dimethylaminophosphonate	2.815	0.043	4
Tributylphosphine sulphide	1.440	0.118	2
Trioctylphosphine sulphide	1.525	0.097	2
Triethyl thiophosphate	0.715	0.046	9
Hexamethylthiophosphoramide	1.305	0.010	7
Diethyl selenide	0.141	0.039	4
Dibutyl selenide	0.219	0.238	2

[a] These values generate the L_A and D_A values for the reference sets given in Table 2.

Table 4. Secondary values of log K_B^H for some bases.

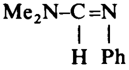
Compound	log K_B^H	Compound	log K_B^H
Propionaldehyde	0.694	Hexa-1,2-diene	−0.63
Ethyl benzoate	0.863	Styrene	−0.27
Furan	−0.420	4-Nitrobenzaldehyde	0.36
Acetic anhydride	1.502	*p*-Benzoquinone	0.49
Pyrrolidin-2-one	2.607	$Me_2N{\cdot}NO$	1.24
Piperidine	2.350	$Ph_2N{\cdot}NO$	0.56
Morpholine	1.860	Propionyl fluoride	−0.14
Triphenylamine	0.246	Benzoyl fluoride	−0.29
Pentafluorobenzonitrile	0.006	$Ph_2P{\cdot}CN$	0.80
$(Me_2N)_2C{=}NH$	3.140	Quinuclidine	2.63
 $\underset{H}{Me_2N{-}C}{=}\underset{Ph}{N}$	1.900	Ferrocene	0.17
Triphenylphosphine	1.107		
Triphenylarsine	0.246		
Thiophene	−0.369		

Table 5. Values of β_2^H for some homologous series of solutes.

n-Homologue	β_2^H	*n*-Homologue	β_2^H
$BuC{\equiv}CH$	0.17	MeCN	0.44
$PeC{\equiv}CH$	0.20	EtCN	0.44
$HexC{\equiv}CH$	0.22	PrCN	0.45
		BuCN	0.44
PhH	0.15		
PhMe	0.14	$PrNH_2$	0.70
PhEt	0.15	$BuNH_2$	0.71
$PhC_{12}H_{25}$	0.17	$PeNH_2$	0.70
		$HexNH_2$	0.69
EtCHO	0.39	$HeptNH_2$	0.69
PrCHO	0.40	$OctNH_2$	0.71
HeptCHO	0.39	$NonNH_2$	0.71
NonylCHO	0.40	$DecNH_2$	0.70
		$OctadecylNH_2$	0.73
Me_2O	0.43		
Et_2O	0.45	Et_3N	0.67
Pr_2O	0.44	Pr_3N	0.58
Bu_2O	0.42	Bu_3N	0.60
Pe_2O	0.46	Pe_3N	0.61
		Oct_3N	0.62
Me_3PO	0.98		
Et_3PO	1.02	Et_2NH	0.70
Pr_3PO	0.99	Pr_2NH	0.71
Bu_3PO	0.93	Bu_2NH	0.71
		Pe_2NH	0.71
$MeCONEt_2$	0.73		
$EtCONEt_2$	0.69		
$PrCONEt_2$	0.71		
$NonylCONEt_2$	0.71		

This effect is quite pronounced with the alkyl-substituted pyridines (Table 8), the maximum effect being shown by 2,6-di(t-butyl)pyridine which has a β_2^H value of only 0.19 as compared with 0.62 for pyridine itself.

In addition to the primary and secondary values of log K_B^H

Table 6. Effect of chain branching on β_2^H.

Solute	β_2^H	Solute	β_2^H
EtOEt	0.45	MeCN	0.44
$EtOPr^n$	0.44	EtCN	0.44
$EtOBu^t$	0.49	Bu^tCN	0.44
Et_2O	0.45	n-(Alkyl)NH_2	0.70
$Pr_2{}^iO$	0.46	Pr^iNH_2	0.72
$Bu_2{}^tO$	0.38	Bu^tNH_2	0.71
MeCOMe	0.50	Me_2S	0.28
MeCOEt	0.48	Et_2S	0.28
$MeCOPr^n$	0.48	$Pr_2{}^iS$	0.31
$MeCOPr^i$	0.46	$Bu_2{}^tS$	0.29
$MeCOBu^t$	0.46		
Bu^tCOBu^t	0.46	Bu^nSBu^n	0.29
		Bu^iSBu^n	0.28
$MeCONMe_2$	0.73	Bu^sSBu^n	0.29
$EtCONMe_2$	0.71	Bu^tSBu^n	0.30
Pr^iCONMe_2	0.73		
Bu^iCONMe_2	0.71		
Bu^tCONMe_2	0.70		

Table 7. Effect of halogen substituents on β_2^H.

Solute	β_2^H	Solute	β_2^H
(Alkyl)$CONEt_2$	0.71	(Alkyl)CN	0.44
$ClCH_2CONEt_2$	0.62	$ClCH_2CN$	0.34
$Cl_2CHCONEt_2$	0.54	Cl_2CHCN	0.27
$Cl_3CCONEt_2$	0.49	Cl_3CCN	0.17
$F_3CCONEt_2$	0.47		
		(Alkyl)NH_2	0.70
$(Alkyl)_2CO$	0.48	$CF_3CH_2NH_2$	0.36
$(ClCH_2)_2CO$	0.35		
$(CF_3)_2CO$	0.20	(Alkyl)$P(O)(OEt)_2$	0.82
		$ClCH_2P(O)(OEt)_2$	0.76
		$Cl_2CHP(O)(OEt)_2$	0.70
		$Cl_3CP(O)(OEt)_2$	0.65

Table 8. Steric effects in the aniline and pyridine series.

Solute	β_2^H	Solute	β_2^H
Aniline	0.38	2-Ethylpyridine	0.60
2-Methylaniline	0.38	4-Ethylpyridine	0.66
3-Methylaniline	0.40	2-Isopropylpyridine	0.50
4-Methylaniline	0.42	4-Isopropylpyridine	0.66
		2-(t-Butyl)pyridine	0.50
Pyridine	0.62	4-(t-Butyl)pyridine	0.66
2-Methylpyridine	0.63	2,6-Dimethylpyridine	0.64
3-Methylpyridine	0.62	2,6-Diethylpyridine	0.58
4-Methylpyridine	0.66	2,6-Di(t-butyl)pyridine	0.19

mentioned above, a number of other $\log K_B^H$ (or β_2^H) values can be obtained for some important compounds. Laurence *et al.*[15] have measured $\log K$ values for a number of alcohols, water, and 4-fluorophenol directly against 4-fluorophenol in tetrachloromethane, from which it is possible to obtain secondary $\log K_B^H$ values in the usual way.* They have also transferred a number of solute basicity values for alcohols and phenols from various other scales to the β_2^H scale (we can denote β_2^H values obtained in this way as tertiary values), so that we now have β_2^H values for a range of these important compounds. Values suggested by Laurence *et al.*[15] are in Table 9. The primary alcohols seem to conform to the pattern shown in Table 5, *i.e.* from propan-1-ol onwards β_2^H is constant at 0.45 units.

The 4-fluorophenol $\log K$ value against 4-fluorophenol itself is, of course, a dimerisation constant of the phenol on forming a linear dimer. In principle, we could use a dimerisation constant for any phenol in tetrachloromethane, together with a known α_2^H acidity value and the known[16] relationship between $\log K$ and $\alpha_2^H \cdot \beta_2^H$ [equation (5)] to calculate a β_2^H value. Unfortunately, dimerisation constants for phenols in tetrachloromethane are exceedingly difficult to determine, because in most cases the predominant species are the monomer and the cyclic trimer.[17,18] Dale and Gramstad[18] managed to obtain $K_2 \simeq 0.1$ dm^3 mol^{-1} for pentafluorophenol in tetrachloromethane; since $\alpha_2^H = 0.76$ we can obtain a very approximate value of 0.02 for β_2^H, *via* equation (5). A number of tertiary β_2^H values for very weak hydrogen-bonding bases can also be estimated using other solute scales, for example that constructed by Koppel and Paju[7] using infra-red shifts of phenol $\Delta\nu(OH)$ in CCl_4. Of course, in order for solute hydrogen-bond basicities to be shifted from one scale to another, it is essential either that the two scales have the same θ-value, or that only bases within a given family are so treated.

$$\log K = 7.354\,\alpha_2^H \cdot \beta_2^H - 1.094 \qquad (5)$$

A selection of β_2^H values for the more important bases is collected in Table 10, using the simplification that β_2^H for a given class of aliphatic homologues is constant. Any of the $\log K_B^H$ values in Tables 3 and 4 can simply be converted into additional β_2^H values *via* equation (4).

Discussion

The β_2^H scale is the most general thermodynamically related scale of solute hydrogen-bond basicities yet constructed. It is connected to Taft's $\log K_{HB}$ solute scale partly because 4-fluorophenol is one of the reference acids (Table 1), and also because β_2^H values for bases studied only against 4-fluorophenol can be calculated as secondary values in the usual way. Thus any base with a pK_{HB} value will automatically be included in our set of β_2^H values. This will be so for all bases, since β_2^H and pK_{HB} give rise to similar Maria–Gal θ values (68 and 70°, respectively).

Other hydrogen-bond solute scales with θ some way away from 68° will be linear with β_2^H only within families, for example the solute scale based on infra-red shifts $\Delta\nu(OH)$ for the reference acid phenol in tetrachloromethane[7] which has[5] a θ value of −20°. We have also noted that the relationship between the β_2^H solute scale with θ = 68° and the solvatochromic β_1 solvent scale, based on the pair of indicators 4-nitroaniline and *N*,*N*-dimethyl-4-nitroaniline (θ = 66°).[5] For non-associated solvents, the β_2^H and β_1 scales are reasonably collinear. However, there is so much random deviation between the two scales (about 0.06 units) that they are certainly not interchangeable. Indeed, it has been suggested that estimation of β_2^H from β_1 or *vice versa* is a very hazardous procedure.[5] Clearly, such estimated values must be regarded as preliminary only.

The connection (or lack of connection) between hydrogen-bond solute basicity, and solute basicity involving full proton transfer was noticed years ago by Taft *et al.*[12] who showed the strong family dependence of pK_{HB} and aqueous pK values. In retrospect this is not surprising, since θ-values for the reference acids 4-fluorophenol/CCl_4 and H_3O^+/H_2O are 70° and −52° respectively.[14] Exactly the same family dependence is observed

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* Similarly the $\log K$ values[19] for complexation of amidines with 4-fluorophenol in CCl_4 can be converted into secondary β_2^H values.

Table 9. Values of β_2^H for some hydroxylic solutes, from Laurence *et al.*[15]

Solute	β_2^H	Solute	β_2^H
Water	0.38	$CH_2{=}CHCH_2OH$	0.41
Methanol	0.41	$CH{\equiv}CCH_2OH$	0.30
Ethanol	0.44	2-Fluoroethanol	0.36
Propan-1-ol	0.45	2-Chloroethanol	0.35
Butan-1-ol	0.46	2-Bromoethanol	0.35
Octan-1-ol	0.46	2,2,2-Trifluoroethanol	0.18
Propan-2-ol	0.47	2,2,2-Trichloroethanol	0.21
t-Butyl alcohol	0.49	Hexafluoro-2-propanol	0.03
Cyclohexanol	0.48	Phenol	0.22
Adamantan-1-ol	0.51	3-Methylphenol	0.24
Benzyl alcohol	0.42	4-Methylphenol	0.24
2-Phenylethanol	0.45	4-Fluorophenol	0.21
Ethylene glycol	0.51[a]	3-Trifluoromethylphenol	0.16
		Pentafluorophenol	0.02[b]

[a] Not statistically corrected. The value of β_2^H with a statistical correction is 0.45 units. [b] This work (see the text).

for β_2^H against p*K*, and so we need detail this no further. We have also constructed a plot of β_2^H against the gas-phase proton affinity (PA) of bases. Again, family-dependent character is observed, there being no correlation of β_2^H with PA across families. Hence the lack of connection between solute hydrogen-bond basicity, and basicity in terms of full proton transfer reflects a fundamental difference, and cannot be explained as a solvent effect as between tetrachloromethane and water.

There are, however, solvent effects on hydrogen-bond basicity. It is commonly observed[13,14] that as a solvent becomes more polar, so the log *K* values for hydrogen-bond complexation become smaller. Whether or not *relative* basicity remains the same is another matter. Our own analysis of complexation against the reference acid 4-fluorophenol,[14] shows that as the solvent changes from cyclohexane or tetrachloromethane to dichloromethane, the θ values decreases from 69–70 to 53°, enough to give rise to family dependent character when the two sets of BDPs are plotted against each other. That is, as the solvent becomes more polar, the hydrogen-bond basicity of ethers will be slightly increased, and that of pyridines and trialkylamines somewhat more increased, in comparison with 'polar' bases such as carbonyl compounds, esters, amides, sulphoxides, *etc.* The magnitude of this enhancement is such that if the polar bases are taken to have the same β_2^H values in tetrachloromethane and dichloromethane, then β_2^H for pyridine would increase from 0.63 to 0.71 units and β_2^H for triethylamine from 0.67 to 0.82 units. These increases probably represent the maximum differences likely to be observed experimentally, because when solvents more polar than dichloromethane (relative permittivity $\varepsilon_r = 8.9$) are used, ion-pair proton-transfer equilibria begin to compete with hydrogen-bond formation. However, the variation of relative basicity with solvent does point out the need to specify not only the reference acid or acids used, but also the solvent. As we have indicated before, the reference acid plus solvent should be regarded as the reference acid system.

Substituent Effects.—For a number of aromatic compounds, there are enough values of log K_B^H available for substituents to allow an analysis in terms of the substituent constants σ_I and σ_R. Not only is it of interest to compare the relative magnitudes of the inductive and resonance contributions both with each other and with values for pK_a of the conjugate acids, but it is possible to use a number of the resulting equations to predict further log K_B^H values. There is insufficient data to deal with 2-substituted anilines, but analyses for 3- and 4-substituents are summarised by equations (5)–(10). Equation (8) reveals an

Table 10. Some values of the solute hydrogen-bond parameter β_2^H.

Solute	β_2^H	Solute	β_2^H
Alkanes	0	Water	0.38
Cycloalkanes	0	Methanol	0.41
Alkenes	0.07	Ethanol	0.44
Alkynes	0.20	Primary alcohols	0.45
Chloroalkanes	0.15	Secondary alcohols	0.47
Bromoalkanes	0.17	Tertiary alcohols	0.49
Iodoalkanes	0.18	Phenol	0.22
Dichloromethane	0.05	3-Methylphenol	0.24
Trichloromethane	0.02	4-Methylphenol	0.24
Tetrachloromethane	0.00	4-Fluorophenol	0.21
Tetrahydrofuran	0.51	Pentafluorophenol	0.02
1,4-Dioxane	0.41[a]	$PrCO_2H$	0.42[b]
R_2O	0.45	$PhCO_2H$	0.42[b]
RCHO	0.40	RSH	0.16
Acetone	0.50	R_2S	0.29
RCOR	0.48	Me_2SO	0.78
Cycloalkanones	0.52	$MeSONMe_2$	0.74
HCO_2R	0.38	$MeSO_2NMe_2$	0.52
$MeCO_2Me$	0.40	R_3PO	0.98
RCO_2R	0.45	$(RO)_3PO$	0.77
RCN	0.44	HMPA	1.00
RNH_2	0.70	RSCN	0.37
R_2NH	0.70	RNCS	0.22
Et_3N	0.67		
R_3N	0.61	4-Bromoaniline	0.34
RNO_2	0.25[b]	$PhNO_2$	0.34
$HCONR_2$	0.66	$PhCONR_2$	0.69
Benzene	0.14	PhSOMe	0.70
Toluene	0.14	Ph_2SO	0.67
Xylenes	0.17	$PhSONMe_2$	0.68
Trimethylbenzenes	0.20	$PhSO_2NMe_2$	0.53
Tetramethylbenzenes	0.20	Ph_3PO	0.92
Pentamethylbenzene	0.21	$(PhO)_3PO$	0.62
Hexamethylbenzene	0.22	Pyridine	0.62
PhR	0.15	2-Methylpyridine	0.63
Biphenyl	0.20	3-Methylpyridine	0.62
Naphthalene	0.21	4-Methylpyridine	0.66
Phenanthrene	0.25	2,6-Dimethylpyridine	0.64
PhF	0.10	2-Ethylpyridine	0.60
PhCl	0.09	4-Ethylpyridine	0.65
PhBr	0.09	2,6-Diethylpyridine	0.58
PhI	0.09	2-(t-Butyl)pyridine	0.50
PhOR	0.26	4-(t-Butyl)pyridine	0.66
Ph_2O	0.24	2,6-Di(t-butyl)pyridine	0.19
PhCHO	0.42	2-Chloropyridine	0.45
PhCOMe	0.51	3-Chloropyridine	0.49
Ph_2CO	0.46	3-Bromopyridine	0.51
PhCN	0.42	3-Cyanopyridine	0.44
$PhNH_2$	0.38	Quinoline	0.63
4-Methylaniline	0.42	Pyrimidine	0.53
4-Fluoroaniline	0.36	Pyridazine	0.64
4-Chloroaniline	0.34	Pyrazine	0.48

[a] Statistically corrected. [b] M. H. Abraham and G. S. Whiting, unpublished work.

$$\log K_B^H\,(\text{3-anilines}) = 0.62 - 1.34\,\sigma_I - 0.87\,\sigma_R \qquad (5)$$
$$r = 0.993 \quad s = 0.04 \quad n = 7$$

$$\mathrm{p}K_a\,(\text{3-anilines}) = 4.56 - 2.58\,\sigma_I - 0.79\,\sigma_R \qquad (6)$$
$$r = 0.997 \quad s = 0.04 \quad n = 7$$

$$\log K_B^H\,(\text{3-anilines}) = -1.39 + 0.46\,\mathrm{p}K_a \qquad (7)$$
$$r = 0.933 \quad s = 0.10 \quad n = 7$$

$$\log K_B^H\,(\text{4-anilines}) = 0.65 - 1.11\,\sigma_I - 1.16\,\sigma_R \qquad (8)$$
$$r = 0.989 \quad s = 0.04 \quad n = 7$$

$$\mathrm{p}K_a\,(\text{4-anilines}) = 4.55 - 2.85\,\sigma_I - 2.99\,\sigma_R \qquad (9)$$
$$r = 0.982 \quad s = 0.14 \quad n = 7$$

Table 11. Substituent parameter coefficients for log K_B^H.

System	σ_I	σ_R	σ_R^+
2-Pyridines	−1.79	nil	
3-Anilines	−1.34	−0.87	
3-Pyridines	−1.30	−0.52	
4-Anilines	−1.11	−1.16	
4-Pyridines	−1.10		−1.04
4-Benzonitriles	−1.02	−0.62	
4-Phenylamidines	−0.94	nil	
4-Benzaldehydes	−0.57	−0.76	

$$\log K_B^H \text{ (4-anilines)} = 1.04 + 0.37\,\mathrm{p}K_a \qquad (10)$$
$$r = 0.966 \quad s = 0.07 \quad n = 7$$

unexpectedly large resonance contribution to log K_B^H (4-anilines). Possibly, the lack of solvation in tetrachloromethane of the substituents containing lone pairs allows a larger resonance effect to occur. Exactly the same phenomenon was observed with respect to the hydrogen-bond acidity of *p*-phenols that we described earlier.[6]

For substituted pyridines, we have enough results to set up equations in all three positions: [equations (11)–(19)]. The

$$\log K_B^H \text{ (2-pyridines)}^* = 1.82 - 1.79\,\sigma_I \qquad (11)$$
$$r = .992 \quad s = 0.19 \quad n = 11$$

$$\mathrm{p}K_a \text{ (2-pyridines)}^* = 5.41 - 11.04\,\sigma_I - 2.55\,\sigma_R \qquad (12)$$
$$r = 0.986 \quad s = 0.56 \quad n = 10$$

$$\log K_B^H \text{ (2-pyridines)}^* = 0.84 + 0.16\,\mathrm{p}K_a \qquad (13)$$
$$r = 0.954 \quad s = 0.15 \quad n = 9$$

$$\log K_B^H \text{ (3-pyridines)} = 1.72 - 1.30\,\sigma_I - 0.52\,\sigma_R \qquad (14)$$
$$r = 0.991 \quad s = 0.07 \quad n = 6$$

$$\mathrm{p}K_a \text{ (3-pyridines)} = 5.17 - 6.30\,\sigma_I - 2.72\,\sigma_R \qquad (15)$$
$$r = 0.999 \quad s = 0.06 \quad n = 7$$

$$\log K_B^H \text{ (3-pyridines)} = 0.64 + 0.21\,\mathrm{p}K_a \qquad (16)$$
$$r = 0.992 \quad s = 0.06 \quad n = 6$$

$$\log K_B^H \text{ (4-pyridines)} = 1.79 - 1.10\,\sigma_I - 1.04\,\sigma_R^+ \qquad (17)$$
$$r = 0.997 \quad s = 0.04 \quad n = 9$$

$$\mathrm{p}K_a \text{ (4-pyridines)} = 5.27 - 5.33\,\sigma_I - 4.33\,\sigma_R^+ \qquad (18)$$
$$r = 0.999 \quad s = 0.10 \quad n = 9$$

$$\log K_B^H \text{ (4-pyridines)} = 0.60 + 0.23\,\mathrm{p}K_a \qquad (19)$$
$$r = 0.993 \quad s = 0.06 \quad n = 9$$

analysis of pK_as of substituted pyridines by Taft[20] leads to equations that are satisfactory agreement with equations (12), (15), and (18). In terms of log K_B^H, and also pK_a, the resonance component becomes steadily more important as the substituent becomes more remote. Indeed, for log K_B^H (2-pyridines) the resonance component is effectively zero. The dominance of the inductive effect in the 2-position is most readily explained as due to the close juxtaposition of the ring nitrogen, with its very steep dipole gradient.

A number of 4-substituted amidines of structure PhN=N(H)NMe$_2$ can be correlated *via* equation (20). Benzaldehydes and benzonitriles yield reasonable correlations, equations (21) and (22).

$$\log K_B^H \text{ (4-amidines)} = 2.00 - 0.94\,\sigma_I \qquad (20)$$
$$r = 0.960 \quad s = 0.10 \quad n = 5$$

$$\log K_B^H \text{ (4-benzaldehydes)} = 0.83 - 0.57\,\sigma_I - 0.76\,\sigma_R \qquad (21)$$
$$r = 0.999 \quad s = 0.02 \quad n = 5$$

$$\log K_B^H \text{ (4-benzonitriles)} = 0.87 - 1.02\,\sigma_I - 0.62\,\sigma_R \qquad (22)$$
$$r = 0.993 \quad s = 0.05 \quad n = 5$$

The very different σ_I/σ_R ratios in equation (21) and equation (22), *viz.* 0.75 and 1.65, respectively, closely reflects the different field and resonance weights of the CHO and CN substituents themselves (CHO, $\sigma_I = 0.30$, $\sigma_R = 0.15$; CN, $\sigma_I = 0.57$, $\sigma_R = 0.08$). Although intuitively reasonable, we can think of no close analogy. More of a puzzle is the σ_I/σ_R ratio itself in equation (21); it is rare that $\sigma_I < \sigma_R$ and quite without precedent in hydrogen-bonding relationships which tend to be σ_I dominated.

It is useful to summarise the pattern of σ_I and σ_R coefficients in the log K_B^H correlations (Table 11). The numerical magnitude of the σ_I coefficient seems to be a function of the separation between substituent and the probe site, with 2-substituents < 3-substituents < 4-substituents. The σ_R coefficients are more irregular, and probably relate to lone-pair polarisibility. It should be borne in mind, however, that the sets of substituents in the various equations are not the same. Furthermore, this substituent analysis is, perforce, restricted to substituents that are themselves not strong enough bases to compete with the probe site. Any such competition will lead to log K_B^H values that reflect hydrogen-bonding at two sites in the molecule.

We have previously described the slopes of the lines obtained on plotting the hydrogen-bond acidity, log K_A^H, against pK_a as pseudo-Brønsted coefficients. In the case of the hydrogen-bond acids, these coefficients varied remarkably from 0.66 for 3-phenols down to 0.05 for carbon acids. Although not covering the same range, the corresponding pseudo-Brønsted coefficients for hydrogen-bond bases also vary, from 0.46 for the 3-anilines down to 0.16 for the 2-pyridines. This may be due to the character of sp^3 nitrogen as against sp^2 nitrogen.

Conclusions

In conclusion, we have set up a scale of solute hydrogen-bond basicity that is derived from Gibbs energies of complexation against a set of reference acids in tetrachloromethane. The scale is quite general against reference acids giving rise to $64 < \theta < 73°$, and in addition includes polar bases against reference acids outside these limits. The reference acids that give rise to $64 < \theta < 73°$ in solvent tetrachloromethane will give much lower θ values in more polar solvents. In such cases, the scale is still operational for polar bases, but the less polar bases such as ethers and, especially pyridines and aliphatic amines will now appear relatively stronger. The defined solute hydrogen-bond basicity scale, log K_B^H, or the equivalent β_2^H, shows marked family-dependent character against full proton transfer basicities such as pK in water or PA in the gas phase. We stress that hydrogen bond basicities are not the same as full proton transfer basicities, and that there is little connection between the two processes across families of bases.

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* Excluding 2-isopropylpyridine and 2-(t-butyl)pyridine.

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