JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 2, 540–552 (1989)

HYDROGEN-BONDING 8.† POSSIBLE EQUIVALENCE OF SOLUTE AND SOLVENT SCALES OF HYDROGEN-BOND BASICITY OF NON-ASSOCIATED COMPOUNDS

MICHAEL H. ABRAHAM,‡ GABRIEL J. BUIST, PRISCILLA L. GRELLIER,
R. ANDREW McGILL, DAVID V. PRIOR, SUSAN OLIVER AND ELIZABETH TURNER
Department of Chemistry, University of Surrey, Guildford GU2 5XH, UK

JEFFREY J. MORRIS AND PETER J. TAYLOR
ICI Pharmaceuticals Division, Mereside Alderley Park, Macclesfied SK10 4TG, UK

PIERRE NICOLET
Laboratoire de Spectrochimie Moleculaire, Faculté des Sciences, 2 rue de la Houssinière, 44072 Nantes, France

PIERRE-CHARLES MARIA AND JEAN-FRANÇOIS GAL
Laboratoire de Chimie Physique Organique, Université de Nice, 06034 Nice, France

JOSÉ-LUIS M. ABBOUD
Consejo Superior de Investigaciones Cientificas, Instituto de Quimica Fisica Rocasolano,
Serrano 119-28006, Madrid, Spain

RUTH M. DOHERTY AND MORTIMER J. KAMLET
Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, MD 20910, USA

WENDEL J. SHUELY
US Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010, USA

AND

ROBERT W. TAFT
Department of Chemistry, University of California, Irvine, CA 92717, USA

ABSTRACT

Using the solvatochromic indicator method, a scale of solvent hydrogen-bond basicity, β_1 (General), has been set up using a series of double regression equations,

$$\nu = \nu_0 + s\pi_1^* + b\beta_1$$

for 11 aniline-type indicators. A similar solvent scale, β_1 (Special), has been constructed by the homomorphic comparison method using only results by Laurence *et al.* on the indicators 4-nitroaniline and 4-nitro-N,N-dimethylaniline. Results are available from our previous work on a general solute scale,

---

† Part 7; M. H. Abraham, P. L. Grellier, D. V. Prior, P. P. Duce, J. J. Morris and P. J. Taylor. *J. Chem Soc., Perkin Trans. 2*, (in press).
‡ Author for correspondence.

0894–3230/89/070540–13$06.50

Received 30 August 1988
Revised September 1988

β_2^{H}, and we have also obtained a special solute scale, β_2 (pK_{HB}) from available log K values for hydrogen-bond complexation of bases with 4-fluorophenol in CCl_4. However, the two solute β_2 scales are virtually identical.

It is shown that there is a general connection between β_1(General) and β_2^{H}, with r = 0·9775 and s.d. = 0·05 for 32 compounds, and between β_1(Special) and β_2^{H}, with r = 0·9776 and s.d. = 0·06 for the same 32 compounds. The latter correlation over 60 compounds yields r = 0·9684 and s.d. = 0·07. However, there are so many compounds in these regressions for which the differences in the solvent and solute β values are larger than the total expected error of 0·07 units that the use of β_1 to predict β_2 or vice versa is a very hazardous procedure. About 70 new β_1 values obtained by the double regression method are also reported.

Basicity is one of the fundamental properties of molecules. Even if restricted to hydrogen-bond basicity, there are hundreds of different physicochemical and biochemical processes in which basicity plays a major role.[1-4] Hence, a number of scales of hydrogen-bond basicity have been suggested. For compounds that are non-self-associated§ (i.e. excluding carboxylic acids, alcohols, etc.) there has arisen the assumption, usually by implication, that in the construction of a scale of hydrogen-bond basicity it is possible to include measurements on bases as bulk solvents in addition to measurements on bases as solutes, that is, in dilute solution. Thus Arnett *et al.*[5] determined, for non-self-associated bases, enthalpies of hydrogen-bond complexation of 4-fluorophenol with bases when the latter were present either as the bulk liquids or as dilute solutions in tetrachloromethane. Koppel and Paju[6] suggested that the infrared stretching frequencies of the phenolic OH group, $\Delta\nu$(PhOH), with solute bases in tetrachloromethane solution can be correlated with the corresponding $\Delta\nu$(MeOD) values against bases as pure bulk solvents,[7] but Makitra and Pirig[8] later used a two-parameter equation for the correlations. Probably the most widely known hydrogen-bond basicity parameter is the β-parameter of Taft and co-workers.[1-4,9] Although originally designated as a solvent parameter,[9,10] the five properties selected for the determination of β included only two solvent basicity properties, together with three solute properties with the bases present in dilute solution in tetrachloromethane.[9]

Whether or not it is possible to include both solvent and solute hydrogen-bond basicities in the same (β) scale has never been demonstrated, and in view of the importance of scales of hydrogen-bond basicity, we thought it timely to compare scales of solvent basicity with scales of solute basicity. A choice of which scales to compare is not arbitrary, because Maria, Gal and co-workers[11,12] have shown that two basicity-dependent properties (BDP) will only generally be linear (that is, will show family-independent characteristics) if the two reference acids used to define the BDPs give rise to similar electrostatic-to-covalent ratios in the two corresponding sets of BDPs. The relative electrostatic-to-covalent ratio in any BDP is given by an angle θ, defined[11] as $\tan^{-1}(S_2/S_1)$, where S_2 and S_1 are the sensitivities of a BDP to the base properties F_1 and F_2 in the multiple regression equation (1). The F_1 and F_2 parameters that characterize the bases were obtained[11] by a principal component analysis of various kinds of BDPs.

$$\mathrm{BDP} = \mathrm{BDP}_0 + S_1F_1 + S_2F_2 \tag{1}$$

There are available two well defined scales of solute hydrogen-bond basicity, both of which

---

§ A precise definition of non-self-association in the present context is difficult to formulate. In practice, we may take compounds with either α or β less than about 0·1 to be non-self-associated; α is a hydrogen-bond acidity parameter.

are obtained from complexation constants, as log K, for the hydrogen-bond process [equation (2)] in tetrachloromethane.

$$B + H{-}A \rightarrow B{\cdots}H{-}A \qquad (2)$$

The most extensive scale is one we have derived[13] from log K values against a set of reference acids, and denoted as log K_B^H. These values may be transformed into a hydrogen-bond solute basicity scale, denoted as β_2^H, through equation (3).† The constants in equation (3) are chosen[13] so that for a solute of zero hydrogen-bond basicity $\beta_2^H = 0$, and for the solute base hexamethylphosphortriamide (HMPA) $\beta_2^H = 1$.

$$\beta_2^H = (\log K_B^H + 1\cdot 1)/4\cdot 636 \qquad (3)$$

A less extensive scale of solute hydrogen-bond basicity is the pK_{HB} parameter of Taft and co-workers[14,15] derived from log K values against the particular reference acid 4-fluorophenol. An equation similar to equation (3)‡ can be used to transform pK_{HB} into a solute hydrogen-bond basicity scale:

$$\beta_2(\mathrm{p}K_{HB}) = (\mathrm{p}K_{HB} + 1\cdot 1)/4\cdot 66 \qquad (4)$$

The Maria–Gal θ values calculated for these two β_2 scales are given in Table 1, together with a value for a β_2 scale based on phenol itself as a reference acid in tetrachloromethane. The three solute θ values are almost the same, and show that if a solvent β_1 scale is to be compared with either β_2^H or β_2(pK_{HB}), the solvent scale must be chosen so that it gives rise to a θ value of round about 65–70°.§ Now by far the most convenient procedure for the determination of a solvent hydrogen-bond scale is the solvatochromic comparison method of Kamlet and Taft.[9] In this procedure, the solvatochromic shift of the absorption maximum, ν_{max}, of a hydrogen-bond acid indicator in a solvent is compared with that of a reference indictor. The two types of indicator chosen were either 4-nitrophenol/4-nitroanisole or 4-nitroaniline/*N*,*N*-diethyl-4-nitroaniline.

Table 1. Values of the Maria–Gal θ angle for some hydrogen-bond basicity properties (from refs 11 and 12)

Reference acid	State of the base	θ°
4-Nitrophenol 4-Nitroanisole	Bulk solvent	2[a]
4-Nitroaniline 4-Nitro-*N*,*N*-dimethylaniline	Bulk solvent	66[a]
$\Delta\nu$(OH) for phenol	Solute in CCl_4	−23 (−17)[b]
4-Fluorophenol, β_2(pK_{HB})	Solute in CCl_4	70[c]
Phenol	Solute in CCl_4	67[c]
Set of selected reference acids, β_2^H	Solute in CCl_4	68[c]

[a] For solvatochromic shifts.

[b] Excluding carbonyl solutes with linear hydrogen bonds.

[c] For log K values for hydrogen-bond complexation, equation (2).

---

† We denote solute scales as β_2, solvent scales as β_1 and the original scale of Kamlet and Taft simply as β.

‡ The factor 4·66 in equation (4) is used so that β_2(pK_{HB}) = 1·0 for HMPA, but for normal purposes pK_{HB} should be transformed into a β scale simply via the factor 4·636.

§ The θ value for the solute scale based on infrared shifts of phenol with bases in tetrachloromethane is around −20° (Table 1), and hence this scale cannot be compared with either of the bulk solvent scales shown in Table 1.

We have examined the $\Delta\nu$ values recorded by Nicolet and Laurence,[16] as an example of a coherent set of data obtained by the same workers under the same conditions, and have calculated θ values for the indicators 4-nitrophenol/4-nitroanisole and 4-nitroaniline/*N*,*N*-dimethyl-4-nitroaniline (see Table 1). It is immediately clear that the θ value for the former indicator set is so far away from the solute value of 67–70° in Table 1 that any β_1 scale based on 4-nitrophenol/4-nitroanisole will not be compatible with the solute β_2 scales with $\theta = 67\text{–}70^\circ$ shown in Table 1. It also follows, as was specifically shown by Nicolet and Laurence,[16] that a β_1 scale using the indicator pair 4-nitrophenol/4-nitroanisole will not be compatible with a β_1 scale using the indicator pair 4-nitroaniline/*N*,*N*-dimethyl-4-nitroaniline (i.e. that family-dependent behaviour will be observed). This is most unfortunate, because 4-nitrophenol is certainly the best indicator to use technically: the absorption peaks have less fine structure and are more Gaussian in shape than those for any aniline-type indicator. However, there is no alternative to these aniline-type indicators for the present purpose, and we now set about the construction of a solvent β_1 scale of hydrogen-bond basicity, based on indicators of the aniline type.

There are two main ways of obtaining β_1 values, and we shall construct solvent scales using each of these methods. In the first procedure we use the double regression method suggested by Kamlet *et al.*,[17] using equation (5), where $\nu(i)$ refers to the band maximum of indicator i in a number of non-self-associated solvents, π_1^* is the solvent dipolarity as found also by the solvatochromic method and β_1 is the required solvent basicity. For consistency, we used only the results of Nicolet and Laurence[16] on *N*,*N*-dimethyl-4-nitroaniline (N) and calculated $\pi_1^*(\text{N})$ from equation (6), in which the two defining points are $\pi_1^* = 0$ for cyclohexane and $\pi_1^* = 1$ for DMSO. We stress that these π_1^* values are for use only in equation (5) in combination with $\nu(i)$ for aniline derivatives, and should not be used to replace any existing π_1^* values.

$$\nu(i) = \nu(i)_0 + s\pi_1^*(\text{N}) + b\beta_1 \qquad (5)$$

$$\pi_1^*(\text{N}) = 8{\cdot}00586 - 0{\cdot}28409\ \nu(\text{N})\dagger \qquad (6)$$

Suppose we have wavenumber band maxima for i aniline-type indicators in a variety of solvents for which $\pi_1^*(\text{N})$ values are available. We then construct a set of i equations, one for each indicator:

$$\begin{aligned} \nu(a) &= \nu(a)_0 + s_a\pi_1^*(\text{N}) + b_a\beta_1 \\ \nu(i) &= \nu(i)_0 + s_i\pi_1^*(\text{N}) + b_i\beta_1 \end{aligned} \qquad (7)$$

We then initiate the analysis with three given β_1 values, taking as standards cyclohexane ($\beta_1 = 0$), acetone ($\beta_1 = 0{\cdot}480$) and hexamethylphosphoramide (HMPA) ($\beta_1 = 1$). Because the output β_1 values are slightly different to the input values, we adjusted the latter so that the output values are exactly as selected above. The set of equations is solved by an iterative method in which β_1 values calculated from each individual equation are averaged at the end of each cycle. Iteration proceeds until the averaged β_1 values are constant to 10^{-4} between successive cycles.

The indicators we have used are listed in Table 2. Note that we have not combined any ν values from different laboratories in collecting data for a given indicator. Because different workers have used slightly different procedures in estimating ν values, and possibly different experimental procedures, we feel strongly that all the ν values for a given indicator should be taken from the same body of data. Hence, for example, we list 4-nitroaniline (I) as three

---

† With ν in $10^3\ \text{cm}^{-1}$

Table 2. Indicators used in this work

No.	Indicator	Ref.
Ia	4-Nitroaniline	10
Ib	4-Nitroaniline	16
Ic	4-Nitroaniline	This work
II	3-Nitroaniline	17
III	2-Nitroaniline	18
IV	2-Nitro-*p*-toluidine	18
V	2-Nitro-*p*-anisidine	18
VI	Ethyl 4-aminobenzoate	17
VIIa	4-Aminoacetophenone	17
VIIb	4-Aminoacetophenone	16[a]
VIII	3,5-Dinitroaniline	17
IXa	4-Nitro-*N*-methyl-aniline	19
IXb	4-Nitro-*N*-methyl-aniline	20
IXc	4-Nitro-*N*-methyl-aniline	16
X	4-Nitro-*N*-ethyl-aniline	19
XI	4-Nitro-*N*-isopropyl-aniline	19
XII	3-Nitro-*N*-ethyl-aniline	17
XIII	4-Nitroso-*N*-methylaniline	16[a]

[a] Additional ν values to those given in ref. 16 have been used.

separate entities (Ia, Ib and Ic), using ν values given by Kamlet *et al.* (Ia),[10] Nicolet and Laurence (Ib)[16] and those determined in this work at the University of Surrey (Ic). Other indicator ν values were taken from later papers by Kamlet and co-workers[10,17–19] and Yokoyama.[20] The only indicator we did not use was *N*-methyl-2-nitroaniline, also studied by Yokoyama.[20] Preliminary regressions showed that the coefficient of β_1 in equation (3) was only —0·093 for this indicator, leading to instability of the entire set of equation (7).‡ Presumably, the almost total lack of hydrogen-bond acidity in *N*-methyl-2-nitroaniline is due to internal hydrogen bonding.

An initial study showed that results from the $ArHN_2$ and ArNHR indicators differed considerably, so two separate sets of calculations were carried out, one for indicators I–VIII and one for indicators IX–XIII. For the $ArNH_2$ indicators in the first set, eleven equations were solved by an iterative procedure to give the regression constants ν_0, s and b in Table 3(i). Also given are the standard error of the estimate, s.d.(ν), the multiple correlation coefficient, r, and the number of solvents used. Similarly, seven equations were solved for the ArNHR indicators, the results being given in Table 3(ii). An analysis via the Maria–Gal equation (1) showed, however, that for the solvent β_1(ArNHR) values the θ value was only 50–60°, significantly less than the θ value of 68–70° for the β_2 scales (Table 1). We therefore did not study the ArNHR indicators any further, and give in Table 4 only the β_1 values derived from the indicator set I–VIII. The numbering of solvents in Table 4 is that given by Nicolet and Laurence,[16] and we denote this general scale as β_1(General).

The second way of determining β_1 is to use just one indicator and its reference, following the original procedure.[9] The β_1 values are derived from the enhanced bathochromic shift, $-\Delta\Delta\nu$, of the longest wavelength transition of an indicator relative to the reference indicator.

---

‡ As the coefficient $b \to 0$, calculated values of $\beta_1 \to 0/0$, leading to enormous errors in the generated β_1 values.

Table 3. Parameters for the regression equation (6)[a]

Type of indicator	Indicator	ν_0[b]	s[c]	b[d]	s.d.(ν)[e]	r[f]	n[g]
(i) $ArNH_2$	Ia	31·03	−2·847	−3·341	0·09	0·9983	25
	Ib	31·09	−2·899	−3·295	0·11	0·9978	45
	Ic	30·91	−2·604	−3·550	0·07	0·9987	17
	II	28·79	−1·240	−3·239	0·10	0·9955	29
	III	26·55	−1·469	−1·276	0·05	0·9980	16
	IV	25·71	−1·543	−1·095	0·05	0·9984	16
	V	24·21	−1·412	−1·002	0·05	0·9977	16
	VI	36·88	−1·020	−3·359	0·10	0·9970	18
	VIIa	33·10	−1·591	−2·418	0·08	0·9972	27
	VIIb	34·97	−1·656	−2·385	0·13	0·9951	19
	VIII	27·39	−0·888	−3·216	0·12	0·9940	29
(ii) ArNHR	IXa	29·19	−3·135	−1·358	0·07	0·9985	26
	IXb	29·27	−3·282	−1·216	0·06	0·9990	18
	IXc	29·31	−3·241	−1·317	0·07	0·9989	29
	X	29·07	−3·205	−1·268	0·04	0·9993	26
	XI	28·89	−3·136	−1·213	0·07	0·9983	26
	XII	27·06	−2·010	−1·368	0·09	0·9951	31
	XIII	26·63	−2·113	−0·627	0·06	0·9981	19

[a] ν values expressed as 10^3 cm^{-1}.
[b] Intercept.
[c] Coefficient for π_1^*.
[d] Coefficient for β_1.
[e] Standard error of estimate.
[f] Coefficient of multiple correlation.
[g] Number of data points.

For consistency we use only the results of Nicolet and Laurence[16] obtained at 25 °C for 4-nitroaniline and 4-nitro-*N*,*N*-dimethylaniline (N). The spectrocopic shifts $-\Delta\Delta\nu(NH_2)$ are defined by equation (8), and lead to values of 92 cm^{-1} in cyclohexane and 2759 cm^{-1} in HMPA, the two standard compounds that have been used to construct the various β scales.

$$-\Delta\Delta\nu(\mathrm{NH_2}) = 0{\cdot}9841\nu(\mathrm{N}) - \nu(\text{4-nitroaniline}) + 3490\ \mathrm{cm}^{-1} \qquad (8)$$

Then, if we take, as usual, $\beta_1 = 0$ for cyclohexane and $\beta_1 = 1$ for HMPA, we can construct a β_1 scale, based just on the two indicators in equation (8), that we denote as β_1(Special):

$$\beta_1(\mathrm{Special}) = \frac{-\Delta\Delta\nu(\mathrm{NH_2}) - 92}{2759 - 92} \qquad (9)$$

These β_1(Special) values are listed in Table 4 for about 100 solvents studied by Nicolet and Laurence.[16]

EXPERIMENTAL

Spectrophotometric measurements at the University of Surrey were carried out using a Pye Unicam SP8-100 Spectrophotometer, equipped with a thermostated cell holder at 25 °C. Measurements were made only after the instrument had warmed up for at least 15 min, and frequent checks of the wavelength accuracy were made with a Holmium glass filter. The estimated accuracy is about ±30 cm^{-1}, with a reproducibility that is slightly better.

Table 4. Comparison of solvent β_1 and solute β_2 hydrogen-bond basicity scales

			β_1		β_2	
No.	Compound	$\pi_1^*(N)$	General	Special	β_2^H	$\beta_2(pK_{HB})$
1	Perfluoromethylcyclohexane	-0·30		-0·05		
2	Perfluorohexane	-0·34		-0·09		
4	Perfluorodecalin	-0·26	-0·17	-0·05		
5	Perfluoro-1-methyldecalin	-0·24		-0·05		
6	2-Methylbutane	-0·12		0·01		
7	n-Pentane	-0·10	-0·03	0·01		
8	Tetramethylsilane	-0·08		0·00		
9	n-Hexane	-0·08	-0·03	0·00		
10	n-Heptane	-0·06	-0·05	0·00		
11	n-Dodecane	0·00		0·01		
12	Cyclohexane[a]	0	0	0	0	0
13	*cis*-Decalin	0·09	0·06	0·03		
15	Tetrachloromethane	0·24	0·05	-0·05		
16	Tetrachloroethene	0·25	0·03	-0·03		
17	Hexafluorobenzene	0·32	0·00	-0·04		
18	Trichloroethene	0·52	0·01	-0·09		
19	Carbon disulphide	0·55				
20	1,4-Difluorobenzene	0·57		-0·06		
22	Fluorobenzene	0·64		-0·02	0·10	
23	1,3-Dichlorobenzene	0·66		-0·07		
24	Chlorobenzene	0·69	0·09	-0·03	0·11	
27	1,2-Dichloroethane	0·77	0·10	0·01		
28	Bromobenzene	0·72	0·14	-0·01	0·07	
29	1,2-Dichlorobenzene	0·76	0·09	-0·02		
30	Iodobenzene	0·78		-0·01	0·17	
31	Diiodomethane	1·01				
33	Trichloromethane	0·73	0·07	-0·08		
34	Dichloromethane	0·77	0·07	-0·06		
35	Tribromomethane	0·84		-0·02		
36	Benzene	0·59	0·10	0·00	0·15	
37	Toluene	0·49	0·15	0·09	0·14	0·13
38	*p*-Xylene	0·41		0·15	0·18	
39	Mesitylene	0·38		0·18	0·20	0·17
40	Prehnitene	0·42		0·21		
41	1-Chlorobutane	0·44	0·14	0·08	0·11	
42	1-Bromobutane	0·52	0·14	0·08	0·20	
43	Iodobutane	0·57		0·04	0·21	
44	Dimethyl disulphide	0·73		0·10		
45	Diethyl disulphide	0·64		0·10		
46	Methyl phenyl sulphide	0·78		0·10		
47	Dimethyl sulphide	0·60		0·19	0·28	
48	Trimethylene sulphide	0·71		0·23	0·26	
49	Pentamethylene sulphide	0·63		0·20	0·28	
50	Diethyl sulphide	0·47		0·28	0·28	0·26
51	Di-n-butyl sulphide	0·37		0·31	0·29	
52	Tetrahydrothiophene	0·68		0·25	0·26	
53	Diisopropyl sulphide	0·38		0·31	0·31	0·30
54	Anisole	0·72	0·23	0·10	0·26	0·26
55	Di(2-chloroethyl) ether	0·80		0·26		

continued

Table 4 (*continued*)

			β_1		β_2	
No.	Compound	π_1^*(N)	General	Special	β_2^H	$\beta_2(pK_{HB})$
56	Dioxolane	0·70		0·33	0·34[b]	0·34[b]
57	1,4-Dioxane	0·56	0·37	0·31	0·41[b]	0·40[b]
58	Dibenzyl ether	0·76	0·38	0·28	0·39	0·39
59	Diethyl ether	0·30	0·42	0·52	0·45	0·45
60	Di-n-butyl ether	0·24	0·39	0·48	0·42	
61	Tetrahydrofuran	0·63	0·49	0·47	0·51	0·51
62	2,2,5,5-Tetramethyltetrahydrofuran	0·32		0·66	0·55	0·54
63	Chloroacetonitrile	1·00		0·14	0·34	0·32
64	Benzonitrile	0·84	0·40	0·35	0·42	0·41
65	Acetonitrile	0·78	0·30	0·35	0·44	0·43
66	Dimethyl cyanamide	0·82		0·43	0·56	0·57
67	Diethyl carbonate	0·46		0·35		
68	Methyl acetate	0·60		0·39	0·40	
69	Ethyl acetate	0·56	0·40	0·41	0·45	0·47
70	Butanone	0·70	0·47	0·51	0·48	0·49
71	Acetophenone	0·84	0·48	0·43	0·51	0·48
72	Acetone[a]	0·71	0·48	0·49	0·50	
73	Cyclohexanone	0·74	0·55	0·53	0·52	0·52
74	Dimethylformamide	0·87	0·68	0·69	0·66	0·68
75	Tetramethylurea	0·80		0·83	0·74	0·73
76	Dimethylacetamide	0·85	0·73	0·79	0·73	0·75
77	*N*-Methylpyrrolidinone	0·90	0·77	0·78	0·77	0·78
78	Dimethyl sulphate	0·80		0·23		
79	Dimethyl sulphite	0·71		0·44		
81	Dimethyl sulphoxide	1	0·76	0·72	0·77	0·78
82	Tetramethylene sulphoxide	1·00		0·74	0·77	
83	Diethyl chlorophosphate	0·74		0·56		
84	Trimethyl phosphate	0·81		0·65	0·76	0·76
85	Triethyl phosphate	0·75	0·69	0·75	0·79	
86	Hexamethylphosphortriamide[a]	0·85	1	1	1	1
87	Pentafluoropyridine	0·53		0·00		
88	2,6-Difluoropyridine	0·78		0·29	0·26	0·26
89	2-Fluoropyridine	0·82	0·44	0·43	0·43	0·44
90	2-Bromopyridine	0·93		0·43	0·43	
91	Pyrimidine	0·88		0·50	0·47[b]	0·47[b]
92	3-Bromopyridine	0·82		0·53	0·51	0·51
93	Pyridine	0·84	0·63	0·65	0·63	0·64
94	Quinoline	0·95		0·56	0·63	0·63
95	4-Methylpyridine	0·80		0·69	0·66	0·67
96	3,4-Dimethylpyridine	0·79		0·73	0·59	
97	2,4,6-Trimethylpyridine	0·67	0·68	0·70	0·69	
98	Tetramethylguanidine	0·75		1·04	0·91	0·91
99	*N*,*N*-Dimethylbenzylamine	0·43	0·55	0·53	0·59	0·57
100	*N*,*N*-Dimethylpiperazine	0·34		0·66	0·64[b]	0·64[b]
101	Triethylamine	0·18	0·54	0·63	0·67	0·65
102	Tri-n-butylamine	0·12	0·42	0·47	0·60	0·57
103	*N*,*N*-Dimethylcyclohexylamine	0·28		0·75	0·70	0·68

[a] Reference compounds, see text. Note that negative β_1 values have no physical significance.
[b] Statistically corrected.

DISCUSSION

All the basicity values we have are given in Table 4, viz. β_1(General), derived from the set of $ArNH_2$ indicators through equation (7); β_1(Special), derived exclusively from the indicator pair 4-nitroaniline/4-nitro-*N*,*N*-dimethylaniline; β_2^H, the general solute hydrogen-bond scale; and $\beta_2(pK_{HB})$, the solute scale derived only from 4-fluorophenol as the reference complexation acid. The average error in the β_1(General) values is 0·034, but this does not include any possible error in the π_1^* values, so that a more reasonable error in β_1(General) is about 0·05 unit. The error in β_1(Special) is almost exactly the same due to the $\pm 135\ \mathrm{cm}^{-1}$ uncertainty in $-\Delta\Delta\nu(NH_2)$. Since log *K* values for reaction (2) can usually be determined to within 0·05 log unit, the error in β_2 should be only ca 0·01. However, this is probably an underestimate and a more realistic error in 0·02 for both β_2^H and $\beta_2(pK_{HB})$. Hence only differences of more than about 0·07 unit between β_1 and β_2 can be considered as significant. It should be noted also that the negative values of β_1 in Table 4 have no physical significance.

Our original intention was to compare the two general scales, β_1(General) and β_2^H, and the two special scales, β_1(Special) and $\beta_2(pK_{HB})$, separately. However, the two β_2 scales are so close that there is no practical difference between them: of 40 solutes (Table 4) there are only two for which the difference between the two β_2 scales is larger than the expected experimental error, and for these solutes the difference is only 0·03 unit. Since we have a larger selection of β_2^H values than $\beta_2(pK_{HB})$ we have therefore restricted our attention to a comparison of the two β_1 scales with β_2^H.

There are 32 compounds for which we have values for all three basicity scales. Regression equations against β_2^H for all 32 compounds are in equations (10) and (11), where *r* is the correlation coefficient, s.d. the standard deviation and *n* the number of points.

$$\beta_1(\text{General}) = -0{\cdot}0066 + 0{\cdot}9564\beta_2^H \tag{10}$$
$$r = 0{\cdot}9775,\ \text{s.d.} = 0{\cdot}051,\ n = 32$$

$$\beta_1(\text{Special}) = -0{\cdot}0917 + 1{\cdot}1107\beta_2^H \tag{11}$$
$$r = 0{\cdot}9776,\ \text{s.d.} = 0{\cdot}059,\ n = 32$$

There is almost the same goodness-of-fit for these two equations, both of which show that there is reasonable correlation between β_1 and β_2^H. Hence for the first time it is established that for basicity properties giving rise to the same Maria–Gal θ values, a scale of solvent hydrogen-bond basicity is colinear with a scale of solute hydrogen-bond basicity within the expected experimental error (0·05 in β_1) for non-self-associated compounds. Whether or not secondary values of β_2^H can usefully be deduced from β_1 values via equation (10) or (11) is another matter. In equation (10) four out of 32 compounds deviate from the regression line by more than 0.07 unit, and seven out of 32 compounds thus deviate in equation (11). For some compounds, there may be logical reasons for deviation, e.g. acetonitrile may be slightly self-associated and tertiary aliphatic amines may be sterically hindered as solvents. Leaving out these compounds, we obtain the equations

$$\beta_1(\text{General}) = -0{\cdot}0049 + 0{\cdot}9796\beta_2^H \tag{12}$$
$$r = 0{\cdot}9917,\ \text{s.d.} = 0{\cdot}032,\ n = 29\ (\text{omit } 65, 101, 102)$$

$$\beta_1(\text{Special}) = -0{\cdot}098 + 1{\cdot}1219\beta_2^H \tag{13}$$
$$r = 0{\cdot}9804,\ \text{s.d.} = 0{\cdot}057,\ n = 29\ (\text{omit } 65, 101, 102)$$

Table 5. Some values of β_2^H calculated via equation (12)

No.	Compound	β_2^H(calc.)
15	Tetrachloromethane	0·04
16	Tetrachloroethene	0·02
17	Hexafluorobenzene	0·00
18	Trichloroethene	0·00
27	1,2-Dichloroethane	0·09
29	1,2-Dichlorobenzene	0·08
33	Trichloromethane	0·06
34	Dichloromethane	0·06

Equation (12) now seems good enough to use for the prediction of β_2^H from β_1(General) and vice versa. However, there are still two compounds out of 29 that deviate by more than 0.07 unit, and we have knowingly left out three compounds already. In our view, it would be dangerous to use equations (10)–(13) for predictive purposes, except possibly within a restricted class of compounds for which it can be ascertained that there are no outliers. Thus we give in Table 5 some calculated values of β_2^H obtained via equation (12) for some weakly basic compounds. These values seem reasonable and could be used, preferably backed up by other estimates, as preliminary results to extend the β_2^H scale. We have also compared β_1(Special) with β_2^H for all 60 compounds for which results are available, equation (14).

$$\beta_1(\text{Special}) = -0{\cdot}0993 + 1{\cdot}1499\beta_2^H \qquad (14)$$
$$r = 0{\cdot}9684,\ \text{s.d.} = 0{\cdot}068,\ n = 60$$

This equation confirms our discussion of equation (11). There is a general connection between the solvent and solute scales, but with so much random deviation that conversion from one scale to the other is extremely hazardous. There are now 15 compounds out of the listed 60 for which the deviation from the regression equation is greater than 0.07 unit. We have been unable to discern any regularity in these discrepancies in terms of chemical type, and can only conclude that there are minor solvent–indicator interactions that are not compensated for, either by the double regression equation (7) or by the 'homomorph method', equations (8) and (9). It should be noted that a deviation in β of 0.05 unit corresponds to a Gibbs energy of only 0·3 kcal mol^{-1}, which is within the scope of a 'minor interaction.'

Determination of further solvent β_1 values

During the course of our work on establishing the double regression equation (5) for indicator Ic (see Table 3), we obtained results on a number of other solvents. In Table 6 are given values of ν(4-nitroaniline) and ν(N) in about 90 solvents, of which the 17 numbered in Table 6 were studied by Laurence *et al.*[16b] There are a number of possible methods of obtaining β_1, one being the homomorphic method, see equations (8) and (9). However, since we had already used some of our results to construct the equation for Ic in Table 3, we proceeded as follows. For the 17 solvents numbered in Table 6 the ν(N) values given are in good agreement with those reported previously.[17] The standard deviation between the two sets is $0{\cdot}06 \times 10^3$ cm^{-1} and the average deviation is only $-0{\cdot}01 \times 10^3$ cm^{-1}. Hence we can calculate π^*(N) from equation (6), and then obtain β_1 from the equation for Ic (Table 3):

$$\nu(\text{Ic}) = 30{\cdot}91 - 2{\cdot}604\pi_1^*(\text{N}) - 3{\cdot}550\beta_1 \qquad (15)$$

Table 6. Determination of β_1 values via the double regression method, equation (15)

No.	Solvent	$\nu(\mathrm{Ic})^a$	$\nu(\mathrm{N})^a$	$\pi_1^*(\mathrm{N})$	β_1
9	n-Hexane	31·31	28·45	−0·077	−0·06
	2,4-Dimethylpentane	31·41	28·50	−0·090	−0·07
	2,2,4-Trimethylpentane	31·25	28·43	−0·071	−0·04
	2,2,4,4,6,8,8-Heptamethylnonane	31·16	28·22	−0·011	−0·06
	n-Hexadecane	30·99	28·15	0·009	−0·03
12	Cyclohexane	31·13	28·18	0·000	−0·06
	1-Dodecyne	30·03	27·29	0·253	0·06
36	Benzene	29·07	26·01	0·617	0·07
41	n-Butyl chloride	29·24	26·54	0·466	0·13
	tert-Butyl chloride	29·54	26·72	0·415	0·08
42	n-Butyl bromide	29·03	26·35	0·520	0·15
33	Trichloromethane	28·72	25·69	0·707	0·10
	Benzyl chloride	28·35	25·51	0·759	0·16
	1,1,1,2,2,3,3-Heptachloropropane	28·69	26·08	0·597	0·19
72	Acetone	27·29	25·71	0·702	0·50
70	Butanone	27·41	25·80	0·676	0·49
	2-Pentanone	27·53	25·89	0·651	0·47
	3-Pentanone	27·42	25·89	0·651	0·51
	2-Heptanone	27·48	25·94	0·637	0·50
	3-Heptanone	27·21	25·84	0·665	0·55
	4-Heptanone	27·32	25·97	0·628	0·55
	2-Octanone	27·51	25·96	0·631	0·49
	2-Nonanone	27·47	25·94	0·637	0·50
	3-Nonanone	27·49	26·03	0·611	0·52
	5-Nonanone	27·47	26·04	0·608	0·52
	2-Undecanone	27·51	26·06	0·602	0·52
	4-Methylpentan-2-one	27·40	25·82	0·671	0·50
	2,4-Dimethylpentan-3-one	27·40	25·97	0·628	0·53
	3-Methylbutan-2-one	27·49	25·92	0·642	0·49
	2,6-Dimethylheptan-4-one	27·64	26·09	0·594	0·49
	Pinacolone	27·29	25·99	0·622	0·56
	Cyclopentanone	27·17	25·51	0·759	0·50
73	Cyclohexanone	27·03	25·48	0·767	0·53
71	Acetophenone	26·99	25·21	0·844	0·49
	2-Methylacetophenone	28·36	25·35	0·804	0·13
	N-Acetylcaprolactam	27·06	25·41	0·787	0·51
	1-(3-Aminopropyl)-2-pyrrolidinone	25·54	24·78	0·966	0·80
	Propylene carbonate	27·06	25·09	0·878	0·44
69	Ethyl acetate	27·90	26·25	0·548	0·45
	Ethyl laurate	28·47	26·74	0·409	0·45
	Methyl cyanoacetate	27·40	25·24	0·835	0·38
	Methyl trimethylacetate	28·21	26·63	0·441	0·44
	Methyl 2-methylbutyrate	28·27	26·58	0·455	0·41
	1-Chlorobutyl acetate	27·66	25·76	0·688	0·41
	Methyl methacrylate	28·12	26·20	0·563	0·37
	2-(Dimethylamino)ethyl methacrylate	27·57	26·02	0·614	0·49
	Ethyl-2,3-dibromopropionate	25·96	26·77	0·401	1·10
	2-Chloropropyl thiolacetate	27·74	25·64	0·722	0·36
	3-Chloropropyl thiolacetate	27·84	25·62	0·727	0·33
	Ethyl acetoacetate	27·40	25·50	0·762	0·43
	Diethyl malonate	27·70	25·84	0·665	0·42
	Diethyl methylmalonate	27·91	25·96	0·631	0·38

Table 6. (*Continued*)

No.	Solvent	$\nu(\mathrm{Ic})^a$	$\nu(\mathrm{N})^a$	$\pi_1^*(\mathrm{N})$	β_1
	Diethyl ethylmalonate	27·93	25·97	0·628	0·38
	Di-n-butyl malonate	27·97	25·97	0·628	0·37
	Dimethyl chloromalonate	27·53	25·41	0·787	0·37
	Diethyl chloromalonate	27·59	25·59	0·736	0·39
	Dimethyl phthalate	27·19	25·19	0·850	0·42
	Diethyl phthalate	27·29	25·35	0·804	0·43
	Di-n-butyl-phthalate	27·43	25·66	0·716	0·45
	Bis(2-ethylhexyl) phthalate	27·70	25·91	0·645	0·43
	Diisodecyl phthalate	27·89	25·96	0·631	0·39
	Diethyl fumarate	27·97	26·08	0·597	0·39
	Dimethyl glutarate	27·59	25·77	0·685	0·43
	Olive oil (37 °C)	28·32	26·86	0·375	0·45
	Penthrane ($CHCl_2CF_2OCH_3$)	29·07	25·94	0·637	0·05
	Enthrane (CHF_2OCF_2CHFCl)	29·15	25·90	0·648	0·02
	Forane ($CHF_2OCHClCF_3$)	29·05	25·72	0·699	0·01
	Halothane ($CF_3CHClBr$)	29·20	25·85	0·662	0·00
	2-Chloroethyl ethyl sulphide	28·38	25·81	0·673	0·22
	2-Chloroethyl n-propyl sulphide	28·45	25·97	0·628	0·23
	2-Chloroethyl n-butyl sulphide	28·52	26·06	0·602	0·23
	2-Chloroethyl isobutyl sulphide	28·78	26·04	0·608	0·15
	2-Chloroethyl isoamyl sulphide	28·83	26·21	0·560	0·18
	2-Chloroethyl n-hexyl sulphide	28·88	26·23	0·554	0·17
	Di-*tert*-butyl disulphide	28·75	26·75	0·406	0·31
	Thioanisole	28·15	25·43	0·781	0·20
74	Dimethylformamide	26·27	25·13	0·866	0·67
76	Dimethylacetamide	26·18	25·10	0·875	0·69
93	Pyridine	26·56	25·16	0·858	0·60
	Dimethyl methylphosphonate	26·09	25·25	0·833	0·75
	Diisopropyl methylphosphonate	26·57	25·80	0·676	0·73
	Diisopropyl phosphite	26·46	25·62	0·727	0·72
59	Diethyl ether	28·65	27·12	0·301	0·42
60	Di-n-butyl ether	28·80	27·25	0·264	0·40
	Di-n-octyl ether	28·90	27·27	0·259	0·37
61	Tetrahydrofuran	27·49	25·96	0·631	0·50
	Bis(2-chloroethoxy)ethane	28·54	25·49	0·764	0·11
	2,6-Dimethylanisole	28·56	26·11	0·588	0·23

[a] This work, values in 10^3 cm^{-1}.

The results are given in Table 6. For the 17 solvents common to Tables 4 and 6 there is good agreement between the β_1 values given in Table 4 and those calculated via equation (15). Further, for various sets of solvents the $\pi_1^*(\mathrm{N})$ and β_1 values in Table 6 are reasonably self-consistent (see, for example, results for the 17 alicyclic ketones). Hence the present method does seem to yield reasonably reliable values of β_1, based on the indicator pair 4-nitroaniline/4-nitro-*N*,*N*-dimethylaniline.

REFERENCES

1. R. W. Taft, J.-L. M. Abboud, M. J. Kamlet and M. H. Abraham, *J. Solution Chem.*, **14**, 153 (1985).
2. M. J. Kamlet, R. M. Doherty, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *ChemTech*, 566 (1986).

3. M. H. Abraham, R. M. Doherty, M. J. Kamlet and R. W. Taft, *Chem. Br.*, **22**, 551 (1986).
4. M. H. Abraham, P. L. Grellier, M. J. Kamlet, R. M. Doherty, R. W. Taft and J.-L. M. Abboud, *Can. J. Chem.*, **66**, 2673 (1988).
5. E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie and P. von R. Schleyer, *J. Am. Chem. Soc.*, **98**, 2365 (1970).
6. I. A. Koppel and A. I. Paju, *Org. React. (USSR)*, **11**, 121 (1974).
7. I. A. Koppel and V. Palm, *Org. React. (USSR)*, **8**, 291 (1971).
8. R. G. Makitra and Ya. N. Pirig, *Org. React. (USSR)*, **17**, 180 (1980).
9. M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, **98**, 377 (1976).
10. M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, **48**, 2877 (1983).
11. P.-C. Maria, J.-F. Gal, J. de Franceschi and E. Fargin, *J. Am. Chem. Soc.*, **109**, 483 (1987).
12. M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris, P. J. Taylor, P.-C. Maria and J.-F. Gal, *J. Phys. Org. Chem.*, **2**, 243–254 (1989).
13. M. H. Abraham, P. L. Grellier, D. V. Prior, J. J. Morris, P. J. Taylor, C. Laurence and M. Berthelot, in preparation.
14. D. Gurka and R. W. Taft, *J. Am. Chem. Soc.*, **91**, 4794 (1969); R. W. Taft, D. Gurka, L. Joris, P. von R. Schleyer and J. W. Rakshys, *J. Am. Chem. Soc.*, **91**, 4801 (1969).
15. J. Mitsky, L. Joris and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 3442 (1972).
16. (a) P. Nicolet and C. Laurence, *J. Chem. Soc., Perkin Trans. 2*, 1071 (1986); (b) C. Laurence, P. Nicolet and M. Helbert, *J. Chem. Soc., Perkin Trans. 2*, 1081 (1986).
17. M. J. Kamlet, M. E. Jones, R. W. Taft and J.-L. M. Abboud, *J. Chem. Soc., Perkin Trans. 2*, 342 (1979).
18. T. Yokoyama, R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, **98**, 3233 (1976).
19. R. R. Minesinger, M. E. Jones, R. W. Taft and M. J. Kamlet, *J. Org. Chem.*, **42**, 1929 (1977).
20. T. Yokoyama, *Aust. J. Chem.*, **29**, 1469 (1976).