

## Polarity and Basicity of Solvents Part 2.<sup>1</sup> Solvatochromic Hydrogen-bonding Shifts as Basicity Parameters

Christian Laurence,\* Pierre Nicolet, and Maryvonne Helbert

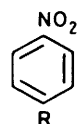
Laboratoire de Spectrochimie moléculaire, Faculté des Sciences, 2 rue de la Houssinière, 44072 Nantes, France

The solvatochromic hydrogen-bonding shifts of *p*-nitrophenol and of *p*-nitroaniline have been measured by the thermosolvatochromic comparison method for an extended sample of oxygen, nitrogen, carbon, halogen, and sulphur bases. Their significance as a hydrogen-bonding parameter has been tested by their correlation with formation constants, n.m.r. shifts, vibrational shifts, and enthalpies for hydrogen-bonding formation. Family-dependent correlations are generally found between the above properties. The correlation of a hydrogen-bonding property for an OH donor *versus* the same property for an NH donor is family (polar oxygen bases, ethers, pyridines, and tertiary aliphatic amines) dependent. The only significant family-independent correlation is for the solvatochromic shift of *p*-nitrophenol *versus* the enthalpy of hydrogen-bond formation of *p*-fluorophenol. It is shown that the  $\beta$  scale is mainly a scale of NH hydrogen-bond acceptor basicity. The averaging process used to define  $\beta$  is criticized and it is recommended that correlation analysis of basicity is undertaken with clearly defined models.

The solvatochromic comparison principle of Kamlet and Taft (KT)<sup>2</sup> enables the solvatochromic shift attributable to hydrogen bonding ( $-\Delta\Delta\bar{\nu}$ ) for polarity–basicity indicators to be disentangled from that attributable to non-specific solvent effects. It leads to a  $\beta$  scale of solvent hydrogen-bond acceptor (HBA) basicity which was given not only the status of a single, highly reliable, basicity parameter in linear solvation energy relationships<sup>3</sup> but also a central role in the correlation analysis of many basicity-dependent properties such as Gibbs energy, enthalpy, or spectral shift associated with the formation not only of hydrogen bonding<sup>2,3</sup> but also of other molecular complexes<sup>4</sup> and even of co-ordination compounds.<sup>5,6</sup> Ultimately it leads to the definition of a new co-ordinate covalency parameter,  $\xi$ , which, when used in combination with  $\beta$ , provides a quantitative norm for the behaviour of oxygen and nitrogen bases in many basicity-dependent properties.<sup>7</sup>

This achievement, a quantitative generalized treatment of basicity, seems so important that it merits the re-examination of its experimental and statistical bases, especially as we have already shown<sup>1</sup> that a certain number of the experimental conditions required for the safe application of the solvatochromic comparison principle were not fulfilled. Furthermore, an examination of the sample of bases used by KT to define the first set of  $\beta$  parameters ( $\beta_{1-5}$ )<sup>2</sup> shows that of the 25 bases studied with the *p*-nitroaniline (3)–*p*-nitro-*NN*-dimethylaniline (5) pair, only a few were nitrogen bases and of the fifteen studied with the *p*-nitrophenol (1)–*p*-nitroanisole (2) pair only one was a nitrogen base. This observation leads us to doubt that the  $\beta$  scale and the equation  $b\beta + e\xi$  apply to all oxygen and nitrogen bases.<sup>†</sup>

In this work we recalculate the  $-\Delta\Delta\bar{\nu}$  values of the two basicity indicators *p*-nitrophenol (1) and *p*-nitroaniline (3) which served to calculate  $\beta_{1-5}$  for 68 bases. Our sample of bases is much more diverse than that of KT as it consists of five aromatic bases, three halogenated bases, ten sulphur bases, 29 oxygen bases, four nitriles, and 17 amines and pyridines. We re-examine the correlations between  $-\Delta\Delta\bar{\nu}(p\text{-nitrophenol})$  and  $-\Delta\Delta\bar{\nu}(p\text{-nitroaniline})$  and those between these two values and (i)  $\log K_f$ , the logarithm of the formation constant for hydrogen-bonding complex formation of *p*-fluorophenol with bases in



(1) R = OH

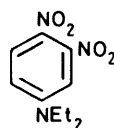
(2) R = OCH<sub>3</sub>

(3) R = NH<sub>2</sub>

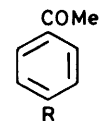
(4) R = NHMe

(5) R = NMe<sub>2</sub>

(6) R = NEt<sub>2</sub>

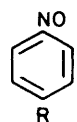


(7)



(8) R = NH<sub>2</sub>

(9) R = NMe<sub>2</sub>



(10) R = NHMe

(11) R = NEt<sub>2</sub>

CCl<sub>4</sub> solution at 25 °C and (ii)  $\Delta$ , the limiting fluorine n.m.r. shift in p.p.m. between complexed and uncomplexed *p*-fluorophenol. KT have claimed that these correlations were 'family independent' (FI) and used them for defining  $\beta_{1-5}$ . We show that this family independence either does not hold or is probably fortuitous because the HBA strengths towards NH donors and OH donors correlate within families of HBA bases but not between families. The  $\beta$  scale thus has no particular virtue compared with other HBA scales.

### Experimental

The drying and purification of HBA solvents used in this work and the spectroscopic procedures have already been described.<sup>1</sup>

<sup>†</sup>  $b$  and  $e$  are the regression coefficients of the correlation between a dependent property and the parameters  $\beta$  and  $\xi$ .

**Table 1.** Wavenumbers ( $10^3 \text{ cm}^{-1}$ ) of the longest wavelength transition of *p*-nitrophenol (1), *p*-nitroanisole (2), *p*-nitroaniline (3), and *p*-nitro-*NN*-dimethylaniline (5) in HBA solvents. Solvatochromic shifts  $-\Delta\Delta\bar{\nu}$  attributable to hydrogen bonding

No.	HBA solvent	$T/^\circ\text{C}$	$\bar{\nu}(1)$	$\bar{\nu}(2)$	$\bar{\nu}(3)$	$\bar{\nu}(5)$	$-\Delta\Delta\bar{\nu}(1) - (2)$	$-\Delta\Delta\bar{\nu}(3) - (5)$		
36	Benzene	25	33.47	32.81	29.09	26.10	193	85		
		50	33.68	32.98	29.33	26.49	161	228		
		75	33.91	33.19	29.59	26.71	150	185		
37	Toluene	0	33.38	32.74	28.93	26.06	210	205		
		25	33.59	32.94	29.19	26.46	209	339		
		50	33.77	33.09	29.44	26.75	186	374		
		75	33.94	33.21	29.69	26.85	141	223		
		105	34.16	33.43	29.92	27.01	150	150		
38	<i>p</i> -Xylene	25	33.64	33.03	29.32	26.74	253	484		
		50	33.85	33.18	29.56	26.88	200	382		
		75			29.79	27.00		270		
39	Mesitylene	105			30.03	27.13		158		
		0	33.27	32.92	29.10	26.70	508	665		
		25	33.55	33.05	29.34	26.85	364	573		
		50	33.77	33.25	29.60	26.95	353	411		
		75			29.82	27.06		299		
40	Prehnitene	105			30.02	27.20		237		
		0			28.90	26.30		471		
		25	33.46	33.05	29.11	26.70	454	655		
		50			29.38	26.85		533		
		75			29.55	26.97		481		
41	<i>n</i> -Butyl chloride	105			29.81	27.09		339		
		25	33.81	33.20	29.38	26.62	260	306		
		42	<i>n</i> -Butyl bromide	25	33.67	33.03	29.13	26.36	223	300
		43	<i>n</i> -Butyl iodide	25			29.04	26.16		194
		44	Dimethyl disulphide	25			28.35	25.62		352
45	Diethyl disulphide	25			28.64	25.91		348		
46	Thioanisole	25			28.15	25.43		365		
47	Dimethyl sulphide	25	33.10	32.91	28.56	26.07	668	585		
48	Trimethylene sulphide	25	32.69	32.50	28.06	25.67	650	691		
49	Pentamethylene sulphide	25	32.91	32.81	28.41	25.95	753	617		
50	Diethyl sulphide	25	33.19	33.07	28.74	26.52	745	848		
51	Di- <i>n</i> -butyl sulphide	25	33.31	33.31	29.02	26.89	875	932		
52	Tetrahydrothiophene	25	32.79	32.68	28.11	25.79	738	759		
53	Di- <i>isopropyl</i> sulphide	25	33.33	33.32	28.98	26.85	866	933		
54	Anisole	25	32.86	32.44	28.35	25.63	417	362		
55	Chloroethyl ether	0	32.30	32.11	27.46	25.23	633	858		
		25	32.49	32.28	27.67	25.37	620	786		
		50			27.96	25.52		644		
		75			28.27	25.65		462		
		105			28.53	25.79		339		
56	Dioxolane	0	32.52	32.46	27.58	25.58	778	1 083		
		25	32.67	32.61	27.81	25.71	785	981		
		50	32.85	32.76	28.11	25.86	761	828		
57	Dioxane	25	32.88	32.94	28.34	26.19	919	923		
		50	33.05	33.09	28.57	26.48	906	978		
		75	33.21	33.23	28.73	26.70	892	1 035		
58	Dibenzyl ether	25	32.11	32.21	27.76	25.51	927	834		
59	Diethyl ether	25	33.22	33.54	28.70	27.11	1 205	1 468		
60	Di- <i>n</i> -butyl ether	0	33.07	33.52	28.70	27.22	1 334	1 577		
		25	33.27	33.70	29.04	27.35	1 322	1 365		
		50	33.42	33.84	29.42	27.49	1 318	1 122		
		75	33.59	33.98	29.80	27.60	1 294	851		
		105	33.81	34.14	30.14	27.89	1 241	796		
61	Tetrahydrofuran	0	32.31	32.64	27.38	25.82	1 176	1 519		
		25	32.48	32.81	27.71	25.97	1 183	1 337		
		50	32.65	32.97	27.86	26.21	1 180	1 423		
62	2,2,5,5-Tetramethyltetrahydrofuran	25	32.94	33.48	28.25	27.05	1 423	1 859		
63	Chloroacetonitrile	0	32.10	31.79	27.09	24.49	499	500		
		25	32.34	31.89	27.28	24.65	364	468		
		50	32.60	31.99	27.42	24.81	208	485		
		75	32.78	32.15	27.55	25.01	195	552		
		105	32.99	32.31	27.76	25.13	152	460		
64	Benzonitrile	25	32.09	32.02	27.29	25.23	749	1 028		
65	Acetonitrile	0	32.47	32.44	27.35	25.32	807	1 057		
		25	32.60	32.53	27.50	25.44	771	1 025		
		50	32.72	32.66	27.63	25.55	787	1 003		
		75			27.84	25.65		892		

Table 1 (continued)

No.	HBA solvent	$T/^\circ\text{C}$	$\bar{\nu}(1)$	$\bar{\nu}(2)$	$\bar{\nu}(3)$	$\bar{\nu}(5)$	$-\Delta\Delta\bar{\nu}(1) - (2)$	$-\Delta\Delta\bar{\nu}(3) - (5)$
66	Dimethylcyanamide	0	31.92	32.22	26.87	25.18	1 128	1 399
		25	32.05	32.31	27.01	25.29	1 092	1 367
		50	32.17	32.43	27.16	25.38	1 097	1 306
		75	32.29	32.52	27.29	25.48	1 071	1 274
		105	32.43	32.68	27.44	25.57	1 098	1 213
67	Diethyl carbonate	25	33.11	33.15	28.58	26.55	908	1 037
68	Methyl acetate	25	32.86	33.03	28.02	26.07	1 033	1 125
69	Ethyl acetate	25	32.90	33.03	28.10	26.21	993	1 183
70	Butanone	25	32.42	32.68	27.36	25.72	1 108	1 441
71	Acetophenone	25			27.09	25.24		1 238
72	Acetone	25	32.50	32.64	27.35	25.67	986	1 401
73	Cyclohexanone	25	32.14	32.37	27.13	25.56	1 064	1 513
74	Dimethylformamide	25	31.43	32.06	26.27	25.11	1 451	1 930
75	Tetramethylurea	25	31.50	32.23	26.14	25.37	1 558	2 316
76	Dimethylacetamide	25	31.33	32.09	26.06	25.18	1 582	2 209
77	<i>N</i> -Methylpyrrolidone	25	31.21	31.92	25.95	25.02	1 525	2 162
78	Dimethyl sulphate	25	32.86	32.44	27.75	25.37	417	706
79	Diethyl sulphite	0	32.44	32.50	27.35	25.58	900	1 313
		25	32.57	32.63	27.51	25.69	906	1 261
		50	32.71	32.76	27.73	25.81	901	1 159
		75	32.86	32.90	28.04	25.93	897	967
		105	33.03	33.06	28.34	26.14	894	874
80	Sulpholane	30	32.12	31.96	26.85	24.77	657	1 016
		50	32.19	32.06	26.95	24.86	649	1 004
81	Dimethyl sulphoxide	25	31.06	31.72	25.75	24.66	1 466	2 007
		50	31.18	31.85	25.87	24.73	1 482	1 956
		75	31.30	31.96	25.97	24.88	1 477	2 004
		105	31.41	32.17	26.14	25.01	1 586	1 962
		25	30.93	31.65	25.68	24.65	1 523	2 068
82	Tetramethylene sulphoxide	25	32.24	32.53	27.08	25.58	1 131	1 583
83	Diethyl chlorophosphate	25	31.89	32.37	26.60	25.33	1 314	1 817
84	Trimethyl phosphate	0	31.72	32.34	26.28	25.42	1 453	2 225
85	Triethyl phosphate	25	31.84	32.46	26.54	25.54	1 458	2 083
		50	31.96	32.61	26.77	25.65	1 495	1 962
		75	32.06	32.73	26.94	25.78	1 520	1 920
		105	32.21	32.90	27.12	25.93	1 547	1 887
		25	30.85	32.03	25.52	25.19	2 000	2 759
86	Hexamethylphosphoramide	50	30.96	32.14	25.60	25.32	2 004	2 807
		75	31.07	32.31	25.68	25.43	2 072	2 835
		105	31.22	32.47	25.81	25.53	2 089	2 804
		0	33.34	32.89	29.08	26.13	407	124
		25	33.62	33.06	29.31	26.33	304	91
87	Pentafluoropyridine	50	33.90	33.18	29.59	26.58	150	57
		75			29.80	26.77		34
		0	32.12	32.17	27.41	25.29	876	967
		25	32.32	32.31	27.64	25.42	822	865
		50	32.50	32.46	27.89	25.52	798	714
88	2,6-Difluoropyridine	75	32.71	32.58	28.22	25.62	713	482
		105	32.93	32.73	28.51	25.76	650	330
		0	31.67	32.02	26.93	25.15	1 169	1 310
		25	31.89	32.22	27.14	25.28	1 158	1 228
		50	32.05	32.33	27.33	25.40	1 113	1 156
89	2-Fluoropyridine	75	32.20	32.46	27.53	25.52	1 098	1 074
		105	32.43	32.64	27.87	25.67	1 056	881
		25	31.34	31.77	26.77	24.91	1 238	1 233
		50			26.77	25.09		1 411
		75			26.97	25.19		1 309
90	2-Bromopyridine	75			27.14	25.36		1 306
		105			27.33	25.50		1 254
		0			26.48	25.16		1 769
		25	31.33	31.97	26.88	25.31	1 457	1 517
		50			27.10	25.45		1 435
91	Pyrimidine	75			27.34	25.55		1 293
		105			27.55	25.69		1 221
		0	30.93	31.89	26.24	25.09	1 774	1 941
		25	31.09	32.04	26.49	25.23	1 770	1 828
		50	31.28	32.16	26.80	25.33	1 705	1 617
92	3-Bromopyridine	75	31.43	32.30	27.00	25.45	1 701	1 535
		105			27.23	25.58		1 433

Table 1 (continued)

No.	HBA solvent	$T/^\circ\text{C}$	$\bar{\nu}(1)$	$\bar{\nu}(2)$	$\bar{\nu}(3)$	$\bar{\nu}(5)$	$-\Delta\Delta\bar{\nu}(1) - (2)$	$-\Delta\Delta\bar{\nu}(3) - (5)$
94	Quinoline	25			26.35	24.84		1 585
95	4-Methylpyridine	25	31.10	32.20	26.51	25.36	1 927	1 936
		50	31.29	32.33	26.81	25.49	1 873	1 764
		75	31.44	32.43	27.03	25.62	1 827	1 672
		105	31.62	32.56	27.29	25.79	1 783	1 579
		0	30.87	31.95	26.10	25.28	1 896	2 268
96	3,4-Dimethylpyridine	25	31.07	32.17	26.43	25.39	1 926	2 046
		50	31.21	32.29	26.76	25.51	1 911	1 834
		75	31.35	32.42	26.96	25.62	1 907	1 742
		105	31.58	32.61	27.20	25.79	1 875	1 669
		0			26.70	25.69		2 071
97	2,4,6-Trimethylpyridine	25	31.41	32.54	26.95	25.82	1 972	1 949
		50	31.60	32.74	27.15	25.97	1 990	1 897
		75	31.77	32.94	27.40	26.18	2 029	1 853
		105	32.05	33.23	27.85	26.50	2 052	1 718
		25			32.35	25.75	25.54	
98	Tetramethylguanidine	25					2 022	1 516
99	<i>NN</i> -Dimethylbenzylamine	25	31.85	33.01	28.21	26.66	2 022	1 516
100	<i>NN</i> -Dimethylpiperazine	0	32.09	33.25	27.78	26.88	2 033	2 162
		25	32.25	33.40	28.21	27.00	2 029	1 850
		50	32.43	33.55	28.49	27.13	2 006	1 698
		75	32.67	33.72	28.73	27.23	1 943	1 557
		0	32.33	33.75	28.46	27.41	2 314	2 004
101	Triethylamine	25	32.50	33.91	28.83	27.56	2 311	1 781
		50	32.71	34.08	29.32	27.76	2 279	1 488
		75	32.88	34.20	29.71	28.00	2 234	1 334
		0	32.31	33.85	28.87	27.62	2 439	1 800
		25	32.46	33.98	29.46	27.76	2 424	1 348
102	Tri- <i>n</i> -butylamine	50	32.61	34.10	29.94	27.93	2 399	1 035
		75	32.70	34.18	30.33	28.08	2 393	793
		105			30.81	28.21		441
		25	32.14	33.57	28.16	27.20	2 316	2 097
		0						

We insist that the use of a very thin cell (30  $\mu\text{m}$ ) allowed us to study 61 of the 68 (90%) bases chosen for *p*-nitroaniline with *p*-nitrophenol (which absorbs at much shorter wavelengths in a region where many solvents are less transparent). It should be noted that KT only achieved a ratio of 60% (15 out of 25) probably due to the use of too thick a cell.

## Results

On the basis of their band shape studied in Part 1,<sup>1</sup> the indicator couples (1)–(2) and (3)–(5) were chosen to establish the scales of HBA basicity *versus* an OH donor and an NH donor, respectively. The wavenumbers of the  $\pi$ - $\pi^*$  transition with the highest wavelength of the indicators (1)–(3) and (5) in solution in the HBA solvents 36–103 are given in Table 1. The  $-\Delta\Delta\bar{\nu}$  shifts attributable to the hydrogen bond of hydrogen-bonding donor (HBD) indicator with the HBA solvents are calculated from equations (1) and (2) established previously<sup>1</sup> and are also

$$-\Delta\Delta\bar{\nu}(1) - (2) = [1.0434 \bar{\nu}(1) - 0.57] - \bar{\nu}(2) \quad (1)$$

$$-\Delta\Delta\bar{\nu}(3) - (5) = [0.9841 \bar{\nu}(3) + 3.49] - \bar{\nu}(5) \quad (2)$$

given in Table 1. The error in these values is the sum of those in each of the terms of the above equations, *i.e.* by taking the error in the first term (in square brackets) as approximately the standard deviation of the corresponding reference line and the error in the second term as 20  $\text{cm}^{-1}$ , 100  $\text{cm}^{-1}$  for  $-\Delta\Delta\bar{\nu}(1) - (2)$ , and 135  $\text{cm}^{-1}$  for  $-\Delta\Delta\bar{\nu}(3) - (5)$ .

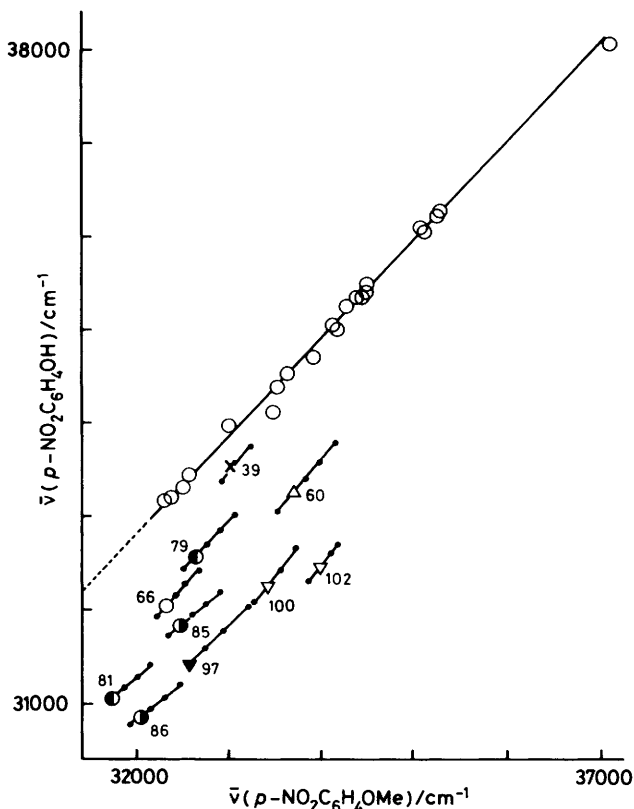
In the correlations which follow, the shifts used are those at 25  $^\circ\text{C}$ . However, for a certain number of HBA solvents the  $-\Delta\Delta\bar{\nu}$  shifts are calculated for several temperatures between 0 and 105  $^\circ\text{C}$ . In fact in the thermosolvatochromic plot<sup>1</sup> the HBA solvents are represented by a temperature curve situated below the reference line. For the pair (1)–(2) these curves are

generally straight lines parallel to the reference line (Figure 1):  $-\Delta\Delta\bar{\nu}(1) - (2)$  remains almost constant with increasing temperature. For the couple (3)–(5) these curves are often straight lines of greater slope than the reference line (Figure 2):  $-\Delta\Delta\bar{\nu}(3) - (5)$  decreases on increasing temperature according to a nearly linear relation as a function of  $1/T$ . In certain cases a more complex temperature curve is observed for the pair (3)–(5), as already seen in the case of the pair (3)–(6) (see Figure 2 of part 1<sup>1</sup>), and which is likely to be attributed to vibrational anomalies). Residues of vibrational anomalies may thus diminish the precision of the  $-\Delta\Delta\bar{\nu}(3) - (5)$  values.

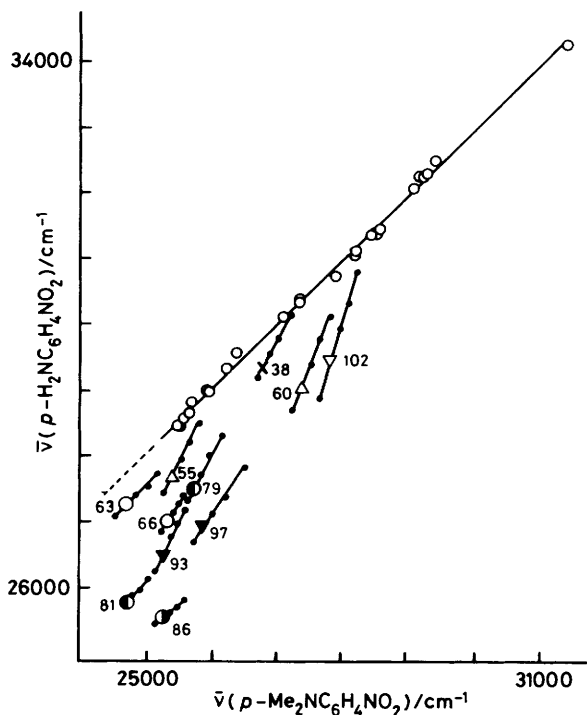
Other quantities characteristic of HBA strength are given in Table 2 and will be discussed later. They are (i) the frequency shift of the  $\nu(\text{OH})$  vibration of methanol caused by hydrogen bonding with the base in  $\text{CCl}_4$  at 20  $^\circ\text{C}$ :  $\Delta\nu(\text{OH}) = \nu(\text{OH})_{\text{free}} - \nu(\text{OH} \cdots \text{B})$  (these values are taken from published<sup>8,9</sup> and unpublished work in our laboratory); (ii)  $\log K_f$  and  $\Delta$ , defined above and taken from the work of Taft *et al.*<sup>10,11</sup>; (iii) the enthalpy of formation of the hydrogen bond of *p*-fluorophenol (PFP) with the bases,  $\Delta H_f(\text{PFP})$ , taken from the calorimetric work of Arnett *et al.*<sup>12,13</sup>; (iv) the enthalpy of formation of the hydrogen bond of *N*-methylaniline with the bases,  $\Delta H_f(\text{PhNHMe})$ , taken from various literature sources.<sup>14–17</sup>

## Discussion

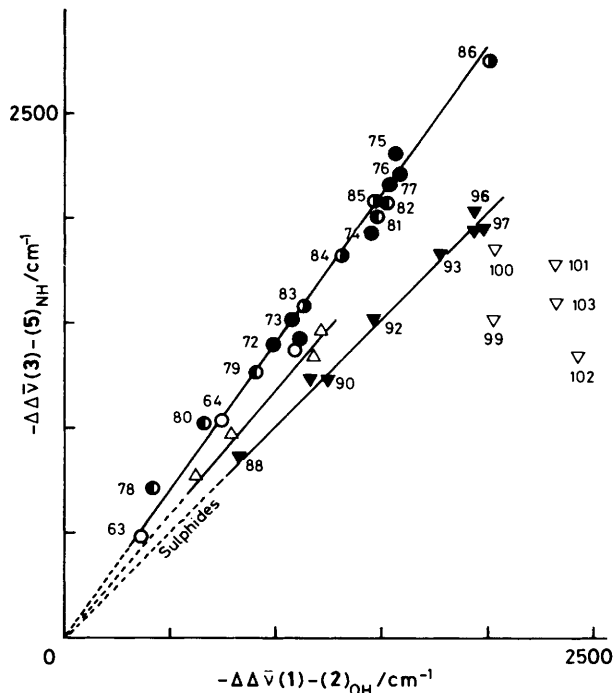
KT have promoted the use of electronic spectral shifts of HBD indicators such as *p*-nitrophenol and *p*-nitroaniline as a measure of HBA strength because they give 'family independent' (FI) correlations<sup>4,7</sup> with each other<sup>2</sup> and with  $\Delta(\text{PFP})$ ,<sup>2</sup>  $\Delta$  (5-fluoroindole),<sup>4,18</sup> and  $\log K_f(\text{PFP})$ .<sup>2</sup> On the other hand<sup>19</sup> they have advised against the use of vibrational spectral shifts of HBD indicators such as methanol and phenol as they give FD correlations<sup>4,7</sup> with the  $\beta$  scale constructed by scaling and averaging the above quantities which give FI correlations. For



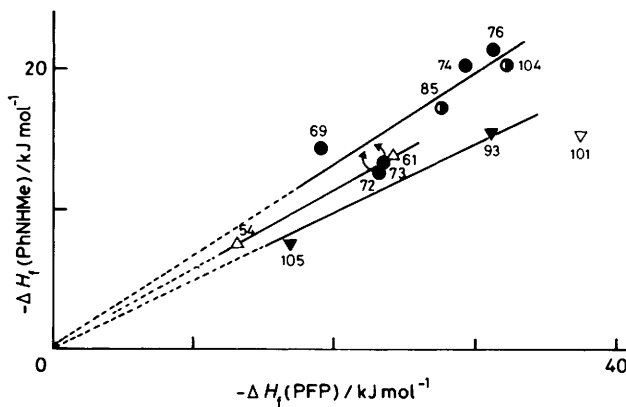
**Figure 1.** Thermosolvatochromic plot for indicators (1) and (2). Numbers refer to Table 1.  $\times$ ,  $\pi$  bases;  $\Delta$ , ethers;  $\nabla$ , amines;  $\blacktriangledown$ , pyridines;  $\bullet$ , SO bases;  $\circ$ , PO bases;  $\circ$ , nitriles (or non-HBA and non-HBD solvents of the reference line)



**Figure 2.** Thermosolvatochromic plot for indicators (3) and (5). The key for symbols is in Figure 1



**Figure 3.** Solvatochromic hydrogen-bonding shifts for *p*-nitroaniline in HBA solvents (key is in Figure 1;  $\bullet$  CO bases) plotted against solvatochromic hydrogen-bonding shifts for *p*-nitrophenol. For the sake of clarity  $\pi$  bases, halogen bases, sulphides, points 67, 68, 69 for CO bases, and 54, 57, 58, 60, and 62 for ethers are not shown



**Figure 4.** Plot of enthalpy of hydrogen-bond formation to *N*-methylaniline versus enthalpy of hydrogen-bond formation to *p*-fluorophenol

the reasons presented in the Introduction, we have re-examined these correlations. Our findings are summarized in Table 3 where we also recall the main results of KT.

*FD Correlations for an NH Donor Property versus the Same OH Donor Property.*—For the correlation of  $-\Delta\Delta\bar{\nu}(1)-(2)$  versus  $-\Delta\Delta\bar{\nu}(3)-(5)$ , Figure 3 and the statistical results of Table 3 show that it is necessary to distinguish four families: (i) the polar bases, mainly oxygen bases (PO, CO, SO, and  $\text{SO}_2$ ) but also nitriles, (ii) ethers, (iii) pyridines (on the line of which

**Table 2.** Properties of hydrogen-bond formation: i.r. shift of methanol,  $\Delta\nu(\text{OH})$  ( $\text{cm}^{-1}$ ),  $^{19}\text{F}$  n.m.r. shift of PFP,  $\Delta(\text{p.p.m.})$ , logarithm of formation constants of PFP complexes,  $\log K_f$ , and enthalpy of formation of PFP complexes,  $\Delta H_f$  (PFP), and of PhNHMe complexes,  $\Delta H_f$  (PhNHMe) ( $\text{kJ mol}^{-1}$ )

No	Bases	$\Delta\nu(\text{OH})^a$	$\Delta^b$	$\log K_f(\text{PFP})^b$	$-\Delta H_f(\text{PFP})^c$	$-\Delta H_f(\text{PhNHMe})^d$
36	Benzene	28			5.15	6.44
37	Toluene	35			5.31	
38	<i>p</i> -Xylene	43				
39	Mesitylene	50			6.69	
40	Prehnitene	56				
41	<i>n</i> -Butyl chloride	24			8.08	
42	<i>n</i> -Butyl bromide	33			7.61	
43	<i>n</i> -Butyl iodide	40			6.49	
44	Dimethyl disulphide	56				
45	Diethyl disulphide	75				
46	Thioanisole	100			6.99	
47	Dimethyl sulphide	137				
48	Trimethylene sulphide	139				
49	Pentamethylene sulphide	146				
50	Diethyl sulphide	146	1.10	0.11	15.19	
51	Di- <i>n</i> -butyl sulphide	148			14.39	
52	Tetrahydrothiophene	154			15.52	
53	Di-isopropyl sulphide	159				
54	Anisole	74		0.36	13.10	7.61
55	Chloroethyl ether	78				
56	Dioxolane	94				
57	Dioxane	126	1.45	0.73	21.34	
58	Dibenzyl ether	129	1.70	0.72	19.20	
59	Diethyl ether	150	1.85	1.01	23.30	
60	Di- <i>n</i> -butyl ether	154				
61	Tetrahydrofuran	158	2.00	1.26	24.06	13.80
62	2,2,5,5-Tetramethyltetrahydrofuran	185				
63	Chloroacetonitrile	49				
64	Benzonitrile	73	1.71	0.80		
65	Acetonitrile	76	1.88	0.90	17.57 <sup>e</sup>	
66	Dimethylcyanamide	118				
67	Diethyl carbonate	76				
68	Methyl acetate	77			17.57	
69	Ethyl acetate	83	1.85	1.09	19.89	14.60
70	Butanone	91	2.02	1.19	21.76	
71	Acetophenone	92	1.92	1.13		12.55
72	Acetone	115			23.39	12.64
73	Cyclohexanone	126	2.12	1.32	23.68	13.47
74	Dimethylformamide	150	2.72	2.06	29.16	20.50 <sup>e</sup>
75	Tetramethylurea	177	3.00	2.42	32.64 <sup>e</sup>	
76	Dimethylacetamide	179	2.86	2.30	31.13	21.59
77	<i>N</i> -Methylpyrrolidone	185	2.91		30.88	
78	Dimethyl sulphate	28			11.80	
79	Diethyl sulphite	75				
80	Sulpholane	81			17.78	
81	Dimethyl sulphoxide	205	2.71	2.53	30.17	
82	Tetramethylene sulphoxide	221	2.80		31.97	
83	Diethyl chlorophosphate	127			23.22	
84	Trimethyl phosphate	173	2.71	2.45	26.94	
85	Triethyl phosphate	189			27.57	17.36 <sup>f</sup>
86	Hexamethylphosphoramide	274	3.71	3.56	36.48	
104	Trimethylphosphine oxide	266			32.22 <sup>e</sup>	20.08 <sup>g</sup>
88	2,6-Difluoropyridine	87				
89	2-Fluoropyridine	167				
90	2-Bromopyridine	192	2.07	0.94	24.39	
91	Pyrimidine	213	1.84	1.05		
92	3-Bromopyridine	241	1.99	1.30	25.94 <sup>e</sup>	
93	Pyridine	286	2.49	1.88	30.96	15.77
94	Quinoline	296	2.40	1.85	31.25	
95	4-Methylpyridine	304	2.70	2.03	31.76	
96	3,4-Dimethylpyridine	316				
97	2,4,6-Trimethylpyridine	349			35.40	
98	Tetramethylguanidine	390	3.70	3.14		

Table 2 (continued)

No.	Bases	$\Delta\nu(\text{OH})^a$	$\Delta^b$	$\log K_f(\text{PFP})^b$	$-\Delta H_f(\text{PFP})^c$	$-\Delta H_f(\text{PhNHMe})^d$
105	<i>NN</i> -Dimethylaniline	244			16.82	7.66
99	<i>NN</i> -Dimethylbenzylamine	397	2.34	1.56		
100	<i>NN</i> -Dimethylpiperazine	402				
101	Triethylamine	429	2.66	1.93	37.32	
102	Tri- <i>n</i> -butylamine	430	2.50	1.57		
103	<i>NN</i> -Dimethylcyclohexylamine	434	2.71	2.08		15.73

<sup>a</sup> In  $\text{CCl}_4$  at 20 °C. <sup>b</sup> In  $\text{CCl}_4$  at 25 °C. <sup>c</sup> In the pure base, unless otherwise stated. <sup>d</sup> In cyclohexane, unless otherwise stated. <sup>e</sup> In  $\text{CCl}_4$ . <sup>f</sup> Value for tri-*n*-butyl phosphate. <sup>g</sup> Value for trioctylphosphine oxide.

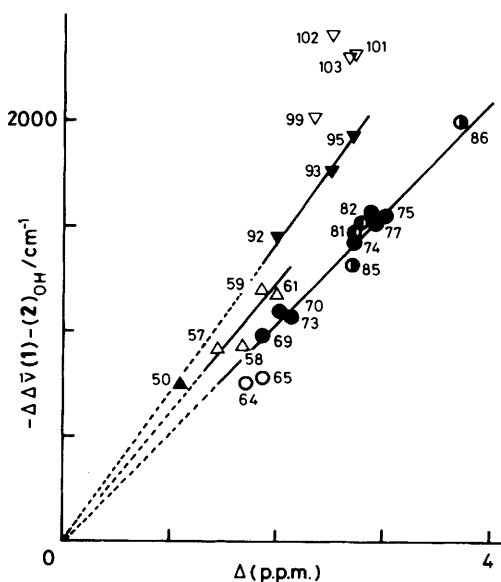


Figure 5. Solvatochromic hydrogen-bonding shifts for *p*-nitrophenol plotted against limiting fluorine n.m.r. shifts for hydrogen-bonded complexes of *p*-fluorophenol with HBA solvents. 2-Bromopyridine is omitted for the sake of clarity

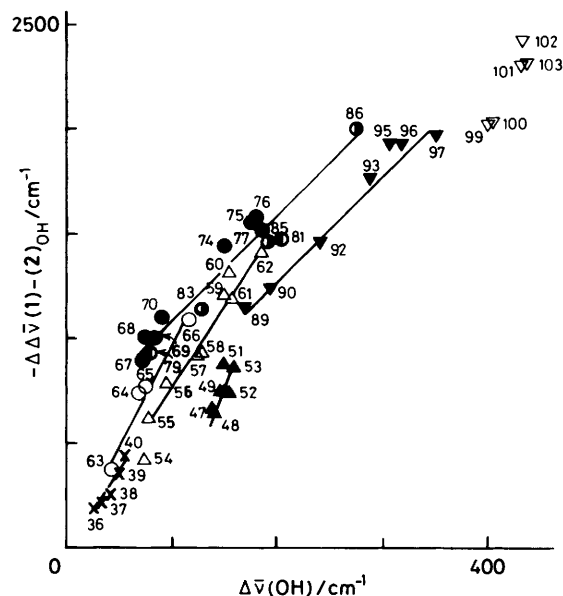


Figure 6. Solvatochromic hydrogen-bonding shifts for *p*-nitrophenol in HBA solvents plotted against shift of the i.r. OH stretching wavenumber of methanol in  $\text{CCl}_4$ . For the sake of clarity a number of points are omitted in each family. Key is as in Figure 1 (●, CO bases; ▲, sulphides)

the sulphides also fall), and (iv) aliphatic tertiary amines. As expected, the lines of the first three families roughly converge at the origin. The location of the weak chloro, bromo, and  $\pi$  bases near the origin, where families merge with one another, prevents their classification.

The family dependence found in Figure 3 is at variance with the results of  $\text{KT}^2$  but is reminiscent of similar behaviour in the plots of (i) i.r.  $\Delta\nu(\text{NH})$  shifts for hydrogen-bonded complex formation with pyrrole *versus* corresponding  $\Delta\nu(\text{OH})$  shifts for methanol complexes; the results of Bellamy and Pace<sup>20</sup> are described by two lines, the upper line for oxygen bases and the lower line for nitrogen bases, and (ii)  $\log K_f$  values for 5-fluoroindole hydrogen-bonded complexes *versus*  $\log K_f$  values for PFP complexes; the results of Taft *et al.*<sup>18</sup> are described by three lines, the upper line for oxygen bases (where benzonitrile falls), the middle line for pyridines, and the lower line for tertiary aliphatic amines; diethyl ether and tetrahydrofuran fall between the oxygen bases and the pyridines.

These results prompt us to study the correlation of the enthalpy of hydrogen-bond formation of an NH donor with that of an OH donor. Literature enthalpy results are scarce for NH donors but the results in Table 2 for *N*-methylaniline are related to a sample of bases just sufficiently diverse to exhibit (Figure 4) an FD correlation for  $-\Delta H_f(\text{PhNHMe})$  and  $-\Delta H_f(\text{PFP})$ : the

upper line refers to oxygen bases (we explain the deviation of acetone and cyclohexanone by the predominance of the angular complex<sup>21</sup> with PFP and of the linear complex<sup>21</sup> with PhNHMe), tetrahydrofuran and anisole define an ether line, pyridine and *NN*-dimethylaniline define a line corresponding to  $sp^2$  or quasi- $sp^2$  nitrogen, and  $\text{NEt}_3$  is below this line.

In conclusion, for four fundamental properties of hydrogen-bond formation, *i.e.* electronic spectral shifts  $-\Delta\Delta\bar{\nu}$ , vibrational shifts  $\Delta\nu$ , Gibbs energy ( $\log K_f$ ), and enthalpy, the correlation between two same properties, the first referring to an NH donor and the second to an OH donor ( $P_{\text{OH}}$  *versus*  $P_{\text{NH}}$ ), is family dependent.

**FD Correlations for  $-\Delta\Delta\bar{\nu}(1) - (2)$  versus  $\log K_f(\text{PFP})$ ,  $\Delta(\text{PFP})$ , and  $\Delta\nu(\text{OH})$ .**—FD correlations are also found for (i)  $-\Delta\Delta\bar{\nu}(1) - (2)$  versus  $\log K_f(\text{PFP})$ , (ii)  $-\Delta\Delta\bar{\nu}(1) - (2)$  versus  $\Delta(\text{PFP})$  (polar bases, ethers, pyridines, and tertiary aliphatic amines are separated as illustrated in Figure 5), and (iii)  $-\Delta\Delta\bar{\nu}(1) - (2)$  versus  $\Delta\nu(\text{OH})$  (the family of polar bases splits into three sub-families, nitriles,  $\text{SO}_2$ , and CO, PO, and SO bases; sulphides become distinguishable from pyridines; Figure 6). Phenomenologically, these FD correlations refer to two different properties, both for an OH donor ( $P_{\text{OH}}$  *versus*  $P'_{\text{OH}}$ ).

Table 3. Correlations between  $-\Delta\Delta\bar{v}(1) - (2)_{\text{OH}}$  ( $\text{cm}^{-1}$ ),  $-\Delta\Delta\bar{v}(3) - (5)_{\text{NH}}$  ( $\text{cm}^{-1}$ ),  $\log K_f$  (PFP),  $\Delta(\text{PFP})$  (p.p.m.),  $\Delta\nu(\text{OH})$  ( $\text{cm}^{-1}$ ), and  $-\Delta H_f$  (PFP) ( $\text{kJ mol}^{-1}$ )

	KT work			This work			Remarks	
	$r^a$	$n^b$	Conclusion	$r^a$	$n^b$	Conclusion		
$-\Delta\Delta\bar{v}(1) - (2)_{\text{OH}}$ vs. $-\Delta\Delta\bar{v}(3) - (5)_{\text{NH}}$ <sup>c</sup>	0.993	15	Family independence (O and N bases)	All HBA $\pi$ Bases PO, SO, SO <sub>2</sub> , CO, C $\equiv$ N bases Ethers Pyridines Sulphides Aliphatic tertiary amines	0.866 0.864 <sup>f</sup> 0.982 0.943 0.994 0.851 <sup>f</sup> g	58 5 23 8 8 6 5	Family dependence. Lines roughly concurrent at the origin	Sulphides on the pyridine line
$-\Delta\Delta\bar{v}(1) - (2)_{\text{OH}}$ vs. $\log K_f(\text{PFP})$	0.972	15	Family independence (O and N bases)	All HBA PO, SO, CO, C $\equiv$ N bases Ethers Pyridines Aliphatic tertiary amines	0.688 0.961 0.931 0.996 g	25 11 5 4 4	Family dependence	Et <sub>2</sub> S on the pyridine line. Subtle distinctions into sub-families not taken into account for polar bases
$-\Delta\Delta\bar{v}(3) - (5)_{\text{NH}}$ vs. $\log K_f(\text{PFP})$	0.979	24	Family independence (O and N bases)	All HBA	0.951	29	Family independence	Fortuitous?
$-\Delta\Delta\bar{v}(1) - (2)_{\text{OH}}$ vs. $\Delta(\text{PFP})$	0.989	10	Family independence (O and N bases)	All HBA PO, SO, CO, C $\equiv$ N bases Ethers Pyridines Aliphatic tertiary amines	0.706 0.977 0.854 <sup>f</sup> 0.924 g	26 13 4 4 4	Family dependence. Lines roughly concurrent at the origin	Et <sub>2</sub> S on the pyridine line
$-\Delta\Delta\bar{v}(3) - (5)_{\text{NH}}$ vs. $\Delta(\text{PFP})$	0.989	15	Family independence (O and N bases)	All HBA	0.957	30	Family independence	Fortuitous?
$-\Delta\Delta\bar{v}(1) - (2)_{\text{OH}}$ vs. $\Delta\nu(\text{OH})$	not studied			All HBA PO, SO, CO bases C $\equiv$ N bases Pyridines $\pi$ Bases Ethers Sulphides Aliphatic tertiary amines	0.932 0.945 0.970 0.989 0.952 0.964 g g	57 17 4 8 5 8 6 5	Family dependence. Lines with (generally) non-zero intercept	
$-\Delta\Delta\bar{v}(3) - (4)_{\text{NH}}$ vs. $\Delta\nu(\text{OH})$ <sup>e</sup>	0.991 0.933 0.974	23 8 6	Family dependence with parallel lines	PO, CO, SO bases Ethers Pyridines	0.950 <sup>h</sup> 0.862 0.960	18 8 10	Family dependence. Lines very roughly concurrent at the origin	
$-\Delta\Delta\bar{v}(1) - (2)_{\text{OH}}$ vs. $\Delta H_f(\text{PFP})$	not studied			All HBA	0.972	37	Family independence	Slight curvature

<sup>a</sup> Correlation coefficient. <sup>b</sup> Number of (data) points. <sup>c</sup>  $-\Delta\Delta\bar{v}(3) - (6)$  in the KT work. <sup>d</sup> In fact  $\beta$ , mainly dependent on  $\Delta\Delta\bar{v}_{\text{NH}}$  in the KT work. <sup>e</sup>  $\Delta\nu(\text{OH})$  phenol in the KT work.  $\Delta\nu(\text{OH})$  methanol in this work. <sup>f</sup> Low correlation coefficient explained by too small a range of  $\Delta\Delta\bar{v}$  values compared with measurement errors. <sup>g</sup> In this family, significant correlations cannot be obtained due to too large a variation in steric effects compared with the variation in electronic effects and too small a range of  $\Delta\Delta\bar{v}$  values compared with measurement errors. <sup>h</sup>  $r$  0.956 if C $\equiv$ N and SO<sub>2</sub> bases are added ( $n$  24).



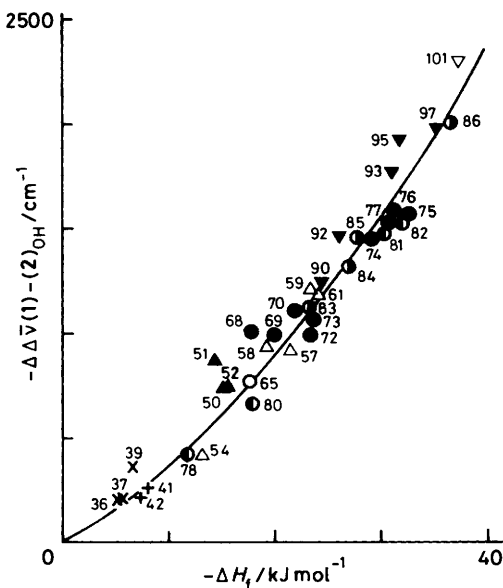
**Table 4.**  $\beta = \Delta\Delta\bar{\nu}_S(i - j)/\Delta\Delta\bar{\nu}_{\text{HMPA}}(i - j)$  for basicity indicators

HBA Solvents		Indicators								$\bar{\beta}_{\text{OH,NH}}^f$	$\bar{\beta}_{\text{NH}}^g$
		(1) - (2)	(3) - (5)	(3) - (6) <sup>a</sup>	(3) - (7) <sup>b</sup>	(4) - (5) <sup>c</sup>	(8) - (9) <sup>d</sup>	(10) - (11) <sup>e</sup>			
Polar HBA	Benzonitrile	0.37	0.37	0.31	0.28	0.52	0.10	0.43	0.34	0.34 ± 0.15	
	Acetonitrile	0.39	0.37	0.32	0.27	0.48	0.25	0.41	0.36	0.35 ± 0.09	
	Dimethyl sulphoxide	0.73	0.73	0.67	0.70	0.83	0.53	0.78	0.71	0.71 ± 0.11	
	Triethyl phosphate	0.73	0.75	0.78	0.78	0.85	0.74	0.81	0.78	0.79 ± 0.04	
	Hexamethylphosphoramide	1	1	1	1	1	1	1	1	1	
Ethers	Dioxane	0.46	0.33	0.30	0.41	0.32	0.34	0.50	0.38	0.37 ± 0.08	
	Di-n-butyl ether	0.66	0.49	0.55	0.57	0.59	0.49	0.41	0.54	0.52 ± 0.07	
Pyridines	2-Fluoropyridine	0.58	0.45	0.39	0.38	0.64	0.21	0.56	0.46	0.44 ± 0.16	
	Pyridine	0.89	0.66	0.63	0.65	0.82	0.42	0.80	0.70	0.66 ± 0.15	
	2,4,6-Trimethylpyridine	0.99	0.71	0.75	0.88	0.91	0.63	0.96	0.83	0.81 ± 0.14	
Amines	Tri-n-butylamine	1.21	0.49	0.51	0.57	0.67	0.42	0.28	0.59	0.49 ± 0.14	
	Triethylamine	1.16	0.65	0.71	0.83	0.87	0.61	0.65	0.78	0.72 ± 0.11	

OH

NH donors

<sup>a</sup> 4-Nitroaniline-*NN*-diethyl-4-nitroaniline. <sup>b</sup> 4-Nitroaniline-*NN*-diethyl-3,4-dinitroaniline. <sup>c</sup> *N*-Methyl-4-nitroaniline-*NN*-dimethyl-4-nitroaniline. <sup>d</sup> 4-Aminoacetophenone-4-dimethylaminoacetophenone. <sup>e</sup> *N*-Methyl-4-nitrosoaniline-*NN*-diethyl-4-nitrosoaniline. <sup>f</sup> Average  $\beta$  values for OH and NH donors. <sup>g</sup> Average  $\beta$  values for NH donors. Standard deviation of the mean calculated with 95% confidence.



**Figure 7.** Solvatochromic hydrogen-bonding shifts for *p*-nitrophenol in HBA solvents plotted against enthalpy of hydrogen-bond formation to *p*-fluorophenol in pure HBA solvent.

**FI Correlations:**  $-\Delta\Delta\bar{\nu}(3) - (5)$  versus  $\log K_f(\text{PFP})$  and versus  $\Delta(\text{PFP})$ .—We confirm the findings of KT<sup>1</sup> that the correlations of  $-\Delta\Delta\bar{\nu}(3) - (5)^*$  versus  $\log K_f(\text{PFP})$  and of  $-\Delta\Delta\bar{\nu}(3) - (5)^*$  versus  $\Delta(\text{PFP})$  are family independent. These FI correlations refer to two different properties for two different classes of donors ( $P_{\text{NH}}$  versus  $P'_{\text{OH}}$ ). We have previously shown that the  $P_{\text{OH}}$  versus  $P_{\text{NH}}$  correlations are FD, as are the  $P_{\text{OH}}$  versus  $P'_{\text{OH}}$  correlations. It may then happen that the correlations of  $P_{\text{NH}}$  with  $P'_{\text{OH}}$  become fortuitously FI by means of a compensation mechanism. In favour of this interpretation, note

\* More exactly  $-\Delta\Delta\bar{\nu}(3) - (6)$  in KT's work.<sup>2</sup>

that the extension of the sample of HBA solvents is detrimental to the quality of the correlations:  $r$  decreases from 0.979 ( $n$  24)<sup>1</sup> to 0.951 ( $n$  29) for  $-\Delta\Delta\bar{\nu}(3) - (5)$  versus  $\log K_f(\text{PFP})$  and from 0.989 ( $n$  15)<sup>1</sup> to 0.957 ( $n$  30) for  $-\Delta\Delta\bar{\nu}(3) - (5)$  versus  $\Delta(\text{PFP})$ .

Moreover, concerning the correlations of  $P_{\text{NH}}$  with  $P'_{\text{OH}}$ , we note that the correlation  $-\Delta\Delta\bar{\nu}(3) - (5)$  versus  $\Delta\nu(\text{OH})$  is FD. However, the families of CO, PO, and SO bases, of ethers, and of pyridines do not separate into parallel lines as claimed by KT<sup>19</sup> but rather into lines roughly convergent to the origin. In fact, for the FI correlations encountered in this work, we never met separations into families of parallel lines. This casts a doubt on the experimental support of the  $b\beta + e\xi$  equation.

**The Enthalpy Dependence of  $-\Delta\Delta\bar{\nu}(1) - (2)$ .**—Finally the FI correlation of highest quality is found between  $-\Delta\Delta\bar{\nu}(1) - (2)$  and  $\Delta H_f(\text{PFP})$  ( $r$  0.972 for 37 bases) (Figure 7). This correlation follows directly from the similarity law:<sup>22</sup> not only are *p*-nitrophenol and *p*-fluorophenol similar OH donors but also both properties are similar, referring more or less to the energy of the hydrogen bond.

This enthalpy dependence of  $-\Delta\Delta\bar{\nu}(1) - (2)$  explains why this quantity remains nearly constant with temperature. In contrast  $-\Delta\Delta\bar{\nu}(3) - (5)$  decreases when the temperature increases and exhibits  $\Delta G$  dependence. Actually,  $-\Delta\Delta\bar{\nu}(3) - (5)$  is correlated with  $\log K_f(\text{PFP})$  but it has been noticed that this correlation may be fortuitous and may have no simple physical significance. 'Van't Hoff plots' of  $-\Delta\Delta\bar{\nu}(3) - (5)$  versus  $1/T$  give slopes which cannot be given a clear interpretation (*e.g.* in the pyridines family, these slopes are not correlated to electronic and/or steric effects of substituents). An explanation remains to be found for the influence of entropy effects on the solvatochromic shifts of NH donors.

**A Caveat against the  $\beta$  Scale.**—KT have claimed<sup>2,4,7</sup> that there exists a set of hydrogen-bonding-dependent properties which give FI correlations with each other: electronic spectral shifts, n.m.r. spectral shifts, and logarithms of formation constants. This claimed FI allowed them to construct a  $\beta$  scale of HBA basicities from the following main steps:<sup>2,3</sup> (i)  $\beta_1$  by scaling enhanced solvatochromic shift for *p*-nitroaniline; (ii)  $\beta_2$

by back-calculation from the correlation of enhanced solvatochromic shift for *p*-nitrophenol versus  $\beta_1$ ; (iii)  $\beta_3$ — $\beta_5$  by back-calculations from the correlations respectively of  $\log K_r(\text{PFP})$ ,  $\Delta(\text{PFP})$ , and  $\log K_r(\text{phenol})$  versus  $\beta_1$ ; (iv)  $\beta_{1-5}$  by averaging  $\beta_1$ — $\beta_5$ ; (v)  $\beta_6$ — $\beta_{13}$  by back-calculations from the correlations of enhanced solvatochromic shifts for eight substituted anilines versus  $\beta_{1-5}$ .

We have shown in this work that the only FI correlation of physical and statistical significance is that for  $-\Delta\Delta\bar{\nu}(1) - (2)$  versus  $\Delta H_r(\text{PFP})$  and that the FI correlations claimed by KT either do not actually hold or are fortuitous. It therefore seems that the  $\beta$  scale has not the degree of generality claimed by its authors. In fact it appears that NH donors weigh heavily in the definition of  $\beta(\beta_1, \beta_6$ — $\beta_{13})$  and that the OH donors intervene either in the case of a biased sample (93% oxygen bases to define  $\beta_2$ ) which does not emphasize their difference with NH donors, or in the case of properties fortuitously related to  $\beta_1$ . It would seem that  $\beta$  is thus more a scale for NH hydrogen-bond acceptor basicity. For example, the  $\beta$  scale predicts that hexamethylphosphoramide (HMPA) is a better hydrogen-bond acceptor than triethylamine; this is so for solvatochromic shifts and enthalpy of formation of hydrogen bonds of NH donors, but the reverse is true for the solvatochromic shifts and the enthalpy of formation of hydrogen bonds of OH donors.

We have another criticism of the method of calculation of  $\beta$  values which averages various physical properties for numerous HBD donors. In Table 4 we report, from indicators studied in Part 1,<sup>1</sup> a set of  $-\Delta\Delta\bar{\nu}$  data which are scaled by  $-\Delta\Delta\bar{\nu}_{\text{HMPA}}$  in order of their comparison with familiar  $\beta$  values.  $\beta$  Values are averaged first for all HBD donors and secondly for NH donors only. From these values it emerges that (i) averaging of inhomogeneous data leads to a loss of information: the first column permits OH donors to be distinguished ( $\beta$  amines  $>$   $\beta$  HMPA) from NH donors ( $\beta$  HMPA  $>$   $\beta$  amines). This information is lost in the average of values. (ii) The standard deviations of the mean  $\beta_{\text{NH}}$  are generally important. We attribute this fact to vibrational anomalies. However, these anomalies are in a certain way systematic, as shown<sup>1</sup> for the couple (3)—(6) and for the nature of the auxochromes on the benzene chromophore. In this case the data are loaded with more or less systematic errors, and the averaging, justified for random errors, is no longer well founded.

The alternative we propose is a choice of indicator couples as free as possible from vibrational anomalies, and with this in

mind we have selected the couples (1)—(2) (OH donor) and (3)—(5) (NH donor). Thus the models are clearly defined and correlation analysis may be undertaken on the basis of the similarity principle.<sup>22</sup>

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