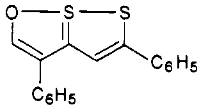
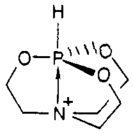
present. This is consistent with the longer S–N bonds to these two nitrogens.

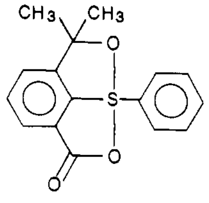
One of the most striking features in **7** is the short S--O "nonbonded" distance of 2.55 Å. Although this distance is clearly much longer than a nominal S–O bond distance of 1.70 Å (sum of covalent radii), it is clearly much shorter than the sum of the van der Waals radii of (3.25 Å).[37] There is, then, a reasonably strong interaction between the S^+ and the O, probably an electrostatic polarization of the oxygen lone pairs by the cationic sulfur. Since the S–N bonds do not have significant multiple-bond character, the lone pairs on oxygen can also interact with the vacant d orbitals on the S^+ further strengthening the S–O interaction. It is probably this S–O interaction that is strongly perturbing the conformation of the eight-membered ring and perhaps the conformations at the nitrogens. The short S--O distance is only 0.20 Å longer than the strong S–O interaction in **17**[38] and is reminiscent of the bonding observed by Verkade and coworkers in compounds like **18**.[39] A similar long S–O bond is found[40] in the tetracoordinated sulfur system **19** where the S–O bond to the carboxylate ligand is 2.25 Å, and the other S–O bond is 1.66 Å. The S–C bonds are of normal length between 1.75 and 1.80 Å.



17



18



19

Registry No. **1**, 105121-46-8; **2**, 105121-47-9; **3**, 85248-37-9; **4**, 96898-10-1; **5**, 79218-01-2; **6**, 91514-28-2; **8**, 105121-50-4; **10**, 91454-72-7; **11**, 53835-21-5; **12**, 105121-48-0; **15**, 70091-69-9; HF_2^-, 18130-74-0; $Me_3SiF_2^-$, 51202-29-0; diphenyldichlorosilane, 80-10-4; chlorotrimethylsilane, 75-77-4; tris(dimethylamino)sulfonium trimethyldifluorosiliconate, 59218-87-0.

Supplementary Material Available: Positional parameters, temperature factors, bond distances and angles, and labeled structures (27 pages); structure factor tables (14 pages). Ordering information is given on any current masthead page.

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Chemometrics of the Solvent Basicity: Multivariate Analysis of the Basicity Scales Relevant to Nonprotogenic Solvents[†]

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Abstract: The dimensionality of the basicity-dependent behavior in the condensed phase, of nonprotogenic organic molecules commonly used as solvents, is approached by a principal component analysis (PCA) of a set of basicity-dependent properties (BDPs) related to hydrogen bonding, proton transfer, and interactions with hard and soft Lewis acids, including the recent $-\Delta H^\circ_{BF_3}$ basicity scale (*J. Phys. Chem.* **1985**, *89*, 1296–1304). By use of the Information theory, the original set of 10 thermodynamic and spectroscopic BDPs was reduced to the 5 most informative scales. This in turn allowed the inclusion of more solvents (22) representing the main classes of nonprotogenic organic media. The first two factors obtained by PCA account for about 95% of the total variance of the data. A physical significance is given to these factors by correlating them with intrinsic gas-phase affinities toward the proton and the potassium ion. A blend of electrostatic and charge-transfer or electron-delocalization characters is attributed to the first factor, which is colinear with proton affinity corrected for enhanced-polarizability effect. The correlation observed between the second factor and the potassium-ion affinity corresponds to an essentially electrostatic character. The third factor, of marginal importance, arises in part from the steric hindrance of complexation (front strain). The relationships between dissimilar BDPs are unraveled in terms of the differences between the sensitivities of the properties to the electrostatic, or long-range, and charge-transfer, or short-range, contributions to the adduct formation. These differences are visualized by a fan-shaped display of the angles $\theta = \tan^{-1} (S_2/S_1)$, associated with the ratio of sensitivities S_2 and S_1 to the second and third factors, respectively. Different BDPs, obtained from the same acid, show a regularity in their θ values, particularly the thermodynamic properties for which the electrostatic character increases in the order $\Delta S^\circ < \Delta H^\circ < \Delta G^\circ$. An explanation is offered for the high charge-transfer character of ΔS° and the conversely high electrostatic character of ΔG°. The Kamlet-Taft β parameter is shown to be a good descriptor of Gibbs free energies of hydrogen bonding.

The most popular word dealing with solvent effects is "polarity", a term not precisely defined, as noted by Reichardt.[1] If we consider, following him, that polarity represents the sum of all those molecular properties responsible for all the interaction forces between solvent and solute molecules, it seems rational that a model proposed to account for solvent effects will include *more*

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than one parameter. Many researchers attempted to explain solvent-dependent properties by using multiple linear regressions (MLR) with various empirical parameters measuring specific and nonspecific interactions between solvent and solute.[2] With this practice, a problem arises from the fact that the possible "explicative" parameters often depend on each other even though they must be independent or at least poorly correlated to give a good significance to the MLR treatment. To circumvent this drawback, two statistical methods of multivariate data analysis leading to *independent* factors, FA for factor analysis and PCA for principal component analysis, were first applied, in the late 1960s, to chemical data. These two methods,[3a,b] equivalent in the way they are used in chemometrics, were, together with the so-called correspondance analysis[3c,d] (CA) (a third method allowing the simultaneous representation of the objects and the variables in the same space), brought into play in the area of liquid properties[4] and solvent effects.[5] Two studies by de Ligny et al.[6] and Swain et al.[7] are to be considered separately, as the authors impose constraints on the factors. It is well established now that the solvent may have at least four effects: dipolarity, polarizability, acidity, and basicity. Most of the previous FA studies attempting to classify solvents or to look at the "dimensionality"[8] of the overall solvent effect included only one basicity scale: DN, the so-called donor number from Gutmann[9] as in the work of Chastrette;[10] B, the $\Delta\nu_{O-D}$ parameter defined by Koppel and Palm[2a] chosen by Elguero et al.[11] or its more recent equivalent $\Delta\nu_{PhOH}$ introduced by Koppel and Paju[12] and used by Bohle et al.[6c] HOMO energies were also used as a substitute for basicity.[13] Only Svoboda et al.[6d] used three basicity scales: DN, B, and β (the solvatochromic parameter introduced by Taft and co-workers).[2b,14] The examination of these studies[6c,d,10,11,13] may lead to the conclusion that only one parameter is sufficient to describe the basicity. Even if one limits the discussion to *solvent* basicity, Drago and co-workers[15] and the Kamlet–Taft group[14,16] have shown that two parameters are necessary to describe thermodynamic and spectral solvent effects in a wide variety of media. Thus, it seems reasonable to return to the original *basicity* data concerning organic molecules commonly used as solvents and to determine their "dimensionality"[17] with as few as possible a priori.[18] So we think it is useful to perform a multivariate analysis of the solvent basicity by using the existing empirical basicity scales determined in the condensed phase.

Data Base

More than 50 basicity-dependent properties (BDPs) were examined.[19]

Since we want to treat matrices without missing data, the number of solvents to be taken into account is drastically reduced due to the low overlapping between the various basicity scales.

A good compromise between a high filling rate (more than 90%) of the data matrix and a set of representative solvents was obtained for 10 BDPs and 22 solvents. Most of the classes of nonprotogenic solvents are represented. The basicity of protogenic solvents depends strongly on their self-association,[20] and very few accurate measurements are available.[21] So protogenic solvents are not taken into account in this work. Also, nonbasic or weakly basic solvents (alkanes, halogenoalkanes, and aromatics) are not included because their interactions with a relatively weak probe reflect mainly *nonspecific* contributions to solvation.

The 10 basicity scales we have selected are based upon thermodynamic (enthalpies or Gibbs free energies) and spectroscopic (vibrational or electronic) measurements by using acids covering a wide range of C_A/E_A or C_A^*/E_A^* ratios.[15] The basic data matrix is shown in Table I. The footnotes in this table give the definitions and the sources of the 10 BDPs constituting the matrix columns.

Whenever possible, values corresponding to a particular BDP were taken from the same source, for the sake of homogeneity. It has been previously pointed out that some DNs ($-\Delta H^\circ_{SbCl_5}$ from the Gutmann's group) appear to be seriously in error.[24,26] They were exchanged for better literature values as tabulated in ref 24. An examination of $-\Delta H^\circ_{I_2}$ found in the literature indicates that

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Table I, Basic Data Matrix[a]

no.[b]	solvent	$-\Delta H^\circ_{BF_3}$[c]	$-\Delta H^\circ_{SbCl_5}$[d]	$-\Delta H^\circ_{I_2}$[e]	$\log K_{I_2}$[f]	$-\Delta H^\circ_{PF}$[g]	pK_{HB}[h]	$\Delta\nu_{PF}$[i]	$\Delta\nu_{PhOH}$[j]	β[k]	$-\Delta H^\circ_i$[l]
3	nitrobenzene	35.79 ± 1.40	8.1 ± 0.7	1.45^m	−1.28 ± 0.18		0.73 ± 0.06	65^m	67	0.39	6.6 ± 0.1
12	acetonitrile	60.39 ± 0.46	14.1 ± 0.35	2.3 ± 0.3	−0.12 ± 0.04	4.2 ± 0.2	0.90 ± 0.06	184	160 ± 3	0.35 ± 0.06	13.6 ± 0.3
25	diethyl carbonate	71.03 ± 0.35	16.0 ± 0.14	2.55 ± 0.2	−0.210 ± 0.036	4.20 ± 0.10	1.00^m	163^m	145 ± 4	0.40	16.4 ± 0.2
31	dioxane	74.09 ± 0.27	14.8 ± 0.37	3.3 ± 0.2	0.150 ± 0.023	5.10 ± 0.11	0.73 ± 0.06	252	237 ± 2	0.37 ± 0.02	21.5 ± 0.2
35	ethyl acetate	75.55 ± 0.31	17.1 ± 0.14	3.0 ± 0.08	−0.027 ± 0.040	4.74 ± 0.12	1.09 ± 0.06	199 ± 5	181 ± 5	0.45 ± 0.02	17.4 ± 0.1
36	acetone	76.03 ± 0.21	17.0 ± 0.11	3.65 ± 0.15	0.049 ± 0.023	5.59 ± 0.08	1.18 ± 0.06	232	224 ± 5	0.48 ± 0.02	18.3 ± 0.1
39	cyclohexanone	76.36 ± 0.82	17.8 ± 0.03	3.7^m	0.1^m	5.66 ± 0.07	1.32 ± 0.06	229	242 ± 2	0.53 ± 0.02	18.1 ± 0.1
45	diethyl ether	78.77 ± 0.38	19.2 ± 0.48	4.2 ± 0.2	−0.016 ± 0.040	5.57 ± 0.12	1.01 ± 0.06	285	280 ± 3	0.47 ± 0.02	19.5 ± 0.7
47	trimethyl phosphate	84.75 ± 0.22	23.0 ± 0.58	2.22	0.590 ± 0.038	6.44 ± 0.09	2.45 ± 0.06	323	305	0.77 ± 0.03	20.4 ± 0.2
50	tetrahydrofuran	90.40 ± 0.28	21.0 ± 0.14	5.3 ± 0.2	0.400 ± 0.040	5.75 ± 0.08	1.26 ± 0.06	292	287 ± 3	0.55 ± 0.02	19.6 ± 0.2
52	2,6-dimethylpyridine	97.73 ± 0.58				8.36 ± 0.12	2.13 ± 0.06	614	535	0.76	40.7 ± 0.3
54	2,4,6-trimethylpyridine	101.03 ± 0.29				8.46 ± 0.11	2.29 ± 0.06	644	531	0.78	42.7 ± 0.2
55	dimethyl sulfoxide	105.34 ± 0.36	29.8 ± 0.75	4.4 ± 0.3	1.250 ± 0.011	7.21 ± 0.08	2.53 ± 0.06	367	362 ± 3	0.76 ± 0.02	28.6 ± 0.2
57	tetramethylurea	108.62 ± 0.22	29.6 ± 0.08	5.2 ± 0.2	1.155 ± 0.027	7.8 ± 0.2	2.30 ± 0.06	350	340	0.78	37.6 ± 0.7
58	*N*,*N*-dimethylaniline	109.16 ± 0.76	28.1^m	8.2 ± 0.3	1.340 ± 0.011	4.02 ± 0.08	0.45 ± 0.06	382 ± 10	422 ± 5		37.7 ± 0.3
59	*N*,*N*-dimethylformamide	110.49 ± 0.18	26.6 ± 0.67	5.0 ± 0.25	0.810 ± 0.038	6.97 ± 0.11	2.06 ± 0.06	305 ± 5	291 ± 3	0.69 ± 0.02	29.5 ± 0.2
62	*N*,*N*-dimethylacetamide	112.14 ± 0.41	27.8 ± 0.09	5.15 ± 0.1	1.180 ± 0.011	7.44 ± 0.13	2.38 ± 0.06	356 ± 5	343 ± 1	0.76 ± 0.02	32.0 ± 0.1
63	*N*-methylpyrrolidone	112.56 ± 0.36	27.3 ± 0.68		1.240 ± 0.011	7.38 ± 0.12	2.37 ± 0.06	339	326^m	0.77 ± 0.03	31.3 ± 0.4
68	hexamethylphosphoramide	117.53 ± 0.45	38.8 ± 0.97	4.8^m	2.02 ± 0.13	8.72 ± 0.11	3.56 ± 0.06	479 ± 10	471 ± 4	1.05 ± 0.06	32.2^m
72	pyridine	128.08 ± 0.50	33.1 ± 0.4	7.47	2.20 ± 0.13	7.40 ± 0.09	1.88 ± 0.06	485 ± 10	472 ± 4	0.64 ± 0.03	38.6 ± 0.3
74	4-methylpyridine	134.17 ± 0.59	34.6^m	8.93	2.56 ± 0.13	7.59 ± 0.08	2.03 ± 0.06	495 ± 10	495 ± 5	0.67	39.0 ± 0.3
75	triethylamine	135.87 ± 1.67	31.7 ± 0.6	12.0	4.04 ± 0.20	8.92 ± 0.09	1.91 ± 0.06	756	650	0.71 ± 0.04	49.1 ± 0.2

[a] Literature data taken at face values (in the original units). [b] Numbering as in ref 24. [c] Heat of complexation with boron trifluoride at 298 K in dichloromethane in kJ·mol^{-1}; quoted errors are confidence limits at the 95% level (CL 95) for 8–12 measurements.[24] [d] Heat of complexation with antimony pentachloride at 298 K in 1,2-dichloroethane in kcal·mol^{-1}, from Gutmann or Olofsson and co-workers; see Table III in ref 24. Uncertainties estimated as follows: 2.5% on Gutmann's data[25] and CL 95 calculated from Olofsson's data. Value for **75** taken from Arnett and co-workers.[26] [e] Heat of complexation with iodine at 298 K in heptane or tetrachloromethane in kcal·mol^{-1} from ref 22 and 27; CL 95 taken from original works when available. [f] Decimal logarithm of the equilibrium constant of complex formation with iodine at 298 K in heptane;[27a,28] CL 95 taken from or evaluated by comparison to ref 27a; by analogy to the scatter on literature values for pyridine,[22] errors are calculated for strong bases **68**, **72**, **74**, and **75**. [g] Heat of hydrogen-bond formation to *p*-fluorophenol by the use of the pure base method, except for **12** and **75**, measured in CCl_4 (high dilution method in agreement when comparisons are possible) and their CL 95 in kcal-mol^{-1}.[29] [h] Decimal cologarithm of the equilibrium constant of hydrogen-bond formation to *p*-fluorophenol in tetrachloromethane; stated precision,[30] 15% on K. [i] IR stretching frequency shifts for the O–H group of *p*-fluorophenol upon hydrogen-bond formation in tetrachloromethane, in cm^{-1};[29b] some values are calculated from IR shifts measured on phenol and methanol. [j] Same definition as (i) but for phenol, average of literature values,[12] uncertainties reflect the scatter in data from different authors. [k] The Kamlet–Taft's hydrogen-bond acceptor parameter[14], CL 95 calculated from primary βi scales when their number equals or exceeds 4 (if less, the βi scatter is given). [l] Heat of transfer of the bases from CCl_4 to HSO_3F and their CL 95 in kcal-mol^{-1}.[29] [m] Our estimations; see text.

Table II, Correlation[a] between the 10 Basicity Scales Used To Build the Basic Data Matrix

$-\Delta H^\circ_{BF_3}$	$-\Delta H^\circ_{SbCl_5}$	$-\Delta H^\circ_{I_2}$	$\log K_{I_2}$	$-\Delta H^\circ_{PFP}$	pK_{HB}	$\Delta\nu_{PFP}$	$\Delta\nu_{PhOH}$	β	$-\Delta H_i$
1	0.96	0.84	0.90	0.95	0.68	0.86	0.90	0.76	0.95
	1	0.70	0.81	0.94	0.82	0.77	0.83	0.86	0.89
		1	0.93	0.78	0.28	0.94	0.93	0.40	0.88
			1	0.87	0.51	0.98	0.98	0.58	0.93
				1	0.79	0.85	0.89	0.86	0.94
					1	0.46	0.51	0.98	0.59
						1	0.99	0.55	0.90
							1	0.61	0.92
								1	0.67
									1

[a] Subset: (13 × 10) including 13 solvents (boldfaced italic numbers in Table II) for which all experimental data are known.

Table III. Independent Factors in Ten-Dimensional Space[a]

	dimensionality									
factors F	1	2	3	4	5	6	7	8	9	10
% variance	82.49	13.96	1.75	0.71	0.57	0.29	0.11	0.06	0.04	0.01
cumulated % variance		96.45	98.21	98.92	99.49	99.79	99.89	99.95	99.99	100.00

variable	correlation coeff[b]			variable	correlation coeff[b]		
$-\Delta H^\circ_{BF_3}$	0.97	0.01	0.20	pK_{HB}	0.72	0.69	-0.11
$-\Delta H^\circ_{SbCl_5}$	0.94	0.24	0.16	$\Delta\nu_{PFP}$	0.93	-0.32	-0.19
$-\Delta H^\circ_{I_2}$	0.86	-0.48	0.05	$\Delta\nu_{PhOH}$	0.95	-0.26	-0.13
$\log K_{I_2}$	0.95	-0.27	-0.11	β	0.79	0.60	-0.09
$-\Delta H^\circ_{PFP}$	0.98	0.14	0.02	$-\Delta H_i$	0.96	-0.12	0.15

[a] For the 13 × 10 subset. [b] Among the three principal factors.

enthalpies measured in heptane and tetrachloromethane are equal within experimental error,[22] leading us to use data obtained in both solvents.

Some of the missing data in the matrix were estimated by using structural considerations, avoiding the use of correlations within the basic data matrix to prevent the introduction of statistical bias.

The experimental uncertainty is one of the variables needed to calculate the amount of information[31] brought by each basic BDP. The uncertainties used in this work, given in Table I, are the confidence limits at the 95% level, whenever available or calculable from the original data. In the absence of such information, either authors' statements about the accuracy of their measurements or the range of literature values from different laboratories is reported.

Methods

Principal Component Analysis. The variables in Table I show widely different ranges and are referenced to various standards. Therefore, PCA was performed on normalized data, and on full matrices, giving equal weight to each column. Calculations were done by using standard methods[32] described elsewhere (see for instance ref 3).

Information Theory. This method, used jointly with PCA, allows optimization of the data matrix through the elimination of the less informative scales, permitting in turn an increase in the number of solvents.

For a set of N solvents, the amount of information (in bits) needed for their *total* discrimination through a particular basicity parameter is obtained via Hartley's formula:[31]

$$I = \log_2 N \tag{1}$$

When the probability of identification (P_i) is less than one (partial discrimination into n subsets), the amount of information contained in one basicity scale is given by Shannon's formula:[31]

$$I = -\sum_{i=1}^{n} p_i \log_2 P_i \tag{2}$$

If N is large, the basicity parameter and the associated error become continuous variables. Normal distributions characterized by their variances σ_b^2 and σ_e^2, respectively, are postulated. Equation 2 leads to eq 3.[33]

$$I = \frac{1}{2} \log_2 \frac{\sigma_b^2}{\sigma_e^2} \tag{3}$$

The variances in eq 3 are estimated from standard deviations s_b and s_e[34] corresponding to the solvents set under study.

Table IV. Classification of the 10 Basicity Scales according to the Decreasing Order of Complementary Amount of Information They Bring in the 13 × 10 Subset

	information			
variable	II[a]	CI[b]	% CCI[c]	% MI[d]
$-\Delta H^\circ_{BF_3}$	3.87	3.87	29	
pK_{HB}	3.08	2.79	50	10
$\Delta\nu_{PFP}$	3.21	2.36	68	26
$-\Delta H_i$	3.55	2.20	84	38
$\Delta\nu_{PhOH}$	3.62	1.25	93	65
β	2.11	0.52	97	75
$-\Delta H^\circ_{PFP}$	2.62	0.40	100	85
$-\Delta H^\circ_{I_2}$	2.16	0		100
$-\Delta H^\circ_{SbCl_5}$	1.90	0		100
$\log K_{I_2}$	1.36	0		100

[a] Individual (II): eq 3, information content of each basicity scale considered as not correlated with the others. [b] Complementary (CI): classification[33] starts from the most individually informative scale (see column 1). [c] % complementary cumulated (% CCI): $\% \text{CCI}_i = \sum_1^i (\text{CI}_i \times 100/\sum_1^{10}\text{CI}_i)$. [d] % mutual: $\% \text{MI}_i = (\text{II}_i - \text{CI}_i)100/\text{II}_i$.

If the information about basicity is supplied by more than one basicity scale, the total amount of information is given by

$$I_{TOT} = \frac{1}{2} \log_2 \frac{|\text{Cov}|_b}{|\text{Cov}|_e} \tag{4}$$

where $|\text{Cov}|_b$ is the determinant of the variance–covariance matrix of the basicity parameters and $|\text{Cov}|_e$ is that of the experimental errors. It seems obvious that the various BDPs are interdependent to some extent. Indeed this is observed for the variance–covariance data matrix or for the corresponding correlation matrix. The redundancy of the information leads us to classify the scales according to their *complementary* information content, using the method of Dupuis and Dijkstra.[33]

Results

A full matrix, containing only experimental values for the 10 basicity scales, was first selected from Table I and subjected to PCA. The 13 solvents subset thus obtained remains representative of the nonprotogenic class. As expected, the corresponding correlation matrix (Table II) shows that many scales are interrelated. Nevertheless, we observe some weak correlations; for example, more than 25% of the correlation coefficients exhibit values below 0.7. Even in this rather restricted context (nonprotogenic solvents) the nonuniqueness of "the basicity" is apparent. The dimensionality is shown in Table III.

Although the first component accounts for more than 82% of the variance in the data, the second factor contributes to the total variance for nearly 14%. At this stage, it may be asked whether the remaining factors are significant. An examination of data errors allows us to consider that the third factor, though mathematically nonsignificant, probably represents not only "noise" but also contains a chemical effect. This will be further emphasized in the study including more solvents. Therefore, the proper number of factors necessary to describe the chemically induced variations in data is at least 2 and at most 3.[35] The

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(31) Eckschlager, K.; Stepanek, V. *Information Theory as Applied to Chemical Analysis*; Wiley: New York, 1979.

(32) Foucart, T. *Analyse Factorielle, Programmation sur Micro-ordinateurs*, 2nd ed.; Masson: Paris, 1985.

(33) Dupuis, F.; Dijkstra, A. *Anal. Chem.* **1975**, *47*, 379-383.

(34) The standard deviation associated with experimental error s_e is generally neither available nor calculable from original data but may be replaced by the CL 95 because the $t/n^{1/2}$ ratio is close to 1 for a number n of measurements near 7 (in data sources cited therein n varies from 5 to 10). For n <5 the standard deviation is well approximated by the range. As the error is not constant over a given scale, the mean error is used to estimate σ_e.

(35) The same conclusion may be reached from the calculation of the factor indicator function.[3a]

Table V. Correlation between the Five Most Informative Scales[a]

$-\Delta H°_{BF_3}$	pK_{HB}	$\Delta\nu_{PFP}$	$-\Delta H_i$	$\Delta\nu_{PhOH}$
1	0.62	0.79	0.89	0.85
	1	0.55	0.53	0.56
		1	0.92	0.98
			1	0.94
				1

[a] All the 22 solvents present in the basic data matrix are considered.

Table VI. Independent Factors in the Space Generated by the Five Most Informative Scales[a]

	dimensionality				
factors F	1	2	3	4	5
% variance	82.14	12.18	4.51	1.00	0.17
cumulated % variance		94.32	98.83	99.83	100.00
variable	correlation coeff[b]				
$-\Delta H°_{BF_3}$	0.92	0.02	0.38		
pK_{HB}	0.69	0.72	−0.09		
$\Delta\nu_{PFP}$	0.95	−0.18	−0.24		
$-\Delta H_i$	0.96	−0.19	0.06		
$\Delta\nu_{PhOH}$	0.97	−0.17	−0.12		

[a] 22 solvents. [b] Among the three principal factors.

correlation coefficients (Table III) represent the coordinates of the 10 basicity scales in the reduced three-dimensional space. The classification of these 10 basicity scales according to Information theory is shown in Table IV.

The most informative scale appears to be $-\Delta H°_{BF_3}$. The strength of the Lewis acid BF_3 gives a range of more than 100 kJ·mol^{-1}. This wide range associated with the good precision of measurements and the careful control of experimental conditions[24] explain the high discriminating power of this basicity scale. pK_{HB} brings the larger amount of information complementary to the preceding (little mutual information). This is in order with the observation of correlation coefficients in Table III. $-\Delta H°_{BF_3}$ values contribute largely to the principal factor and not to the second factor, whereas pK_{HB} contributes the most to the second factor and the least to the first one. The first 7 scales in Table IV provide the same amount of information as the 10 initially selected. If we consent to a loss of 4% and 3% of complementary information brought by β and $-\Delta H°_{PFP}$, respectively, the solvent set can be enlarged to 22.[36] Some important solvents of low basicity, **3** and **25**, or of high basicity, **68**, are now taken into account. Hindered pyridines, **52** and **54**, as well as substituted aniline, **58**, are also included. Results of the PCA run on the 5 remaining basicity scales and the 22 solvents of the original data matrix are shown in Tables V and VI. Redundancy of information has been reduced; 40% of the correlation coefficients are now below 0.7.

The variance explained by the first factor remains almost constant (near 82%). The most noticeable change affects the third factor which gains weight as new solvents are introduced. This gain is obtained in part at the expense of the second factor. Contributions to the third factor appear more clearly, arising from the $-\Delta H°_{BF_3}$ scale and to a less extent from the $\Delta\nu_{PFP}$ scale (anticorrelated to F_3). The coordinates of the 22 solvents along the three principal factors are given in Table VII.

Physical Significance of the Three Principal Factors

A physical significance is clearly distinguishable for the first two of the three principal factors arising from PCA. As shown by correlation coefficients in Table VI, the two most informative scales, $-\Delta H°_{BF_3}$ and pK_{HB}, bring the greatest contributions to the first and second factors, respectively ($-\Delta H°_{BF_3}$ is quasi-orthogonal with F_2, pK_{HB} is the scale most correlated with F_2 and least correlated with F_1). Therefore, the first factor contains chemical effects already evidenced for $-\Delta H°_{BF_3}$, i.e., a blend of covalent and electrostatic characters.[24] Since pK_{HB} is one of the first five basicity scales[41] from which β was averaged, the significance of β, predominantly electrostatic in nature,[42] serves to characterize the second factor. We did not find significant relationships between F_1 or F_2 and various combinations of solvent molecular parameters that are supposed to describe acid–base interactions in terms of charge and frontier control.[43] On the other hand, we obtained meaningful correlations with intrinsic basicity scales in the gas phase: proton affinities, PA, are well explained by F_1 and molecular polarizabilities (α(ahc))

$$PA = (102.2 \pm 6.7)F_1 + (6.5 \pm 1.1)\alpha + 815.3 \qquad (5)$$

The data and units are in Table VII: number of solvents, n = 18; correlation coefficient, r = 0.9828; standard deviation, s = 11.0.[44]

Morokuma has applied his interaction energy decomposition scheme[45] to some proton affinities. The largest components of PA, electron delocalization or charge-transfer (CT) and electrostatic (ES) interactions, are of similar magnitude and polarization (PL) of less importance. We believe that condensed-phase basicities used here, measured toward neutral acids, are less dependent on polarizability than PA. The same is true for the protonation by HSO_3F ($-\Delta H_i$) where the positive charge is partly dispersed in the ion pair and less able to induce polarization.[46] PA, once corrected for enhanced polarizability, gives a physical sense of empirical nature to the abstract factor F_1. Using the terminology of theoretical chemistry (Morokuma), we can state that F_1 appears as a blend of electrostatic (ES) and electron-delocalization or charge-transfer (CT) contributions to the acid–base interaction. Following the approach used above, a logical step was to look for an empirical descriptor of electrostatic interaction to characterize F_2. The bonding of organic bases to alkali-metal cations is largely governed by electrostatic interaction.[38,47] Kebarle and co-workers[38] have determined potassium-ion affinities, KA, for a number of bases which overlap our set for eight representative solvents.[48] Indeed KA is collinear with F_2:

$$KA = (143.1 \pm 18.1)F_2 + 110.5 \qquad (6)$$

The data and units are in Table VII; n = 8; r = 0.9553; s = 7.3.

Contrary to the case of eq 5, the introduction of a polarizability term in the KA relationship did not improve the fit. It is possible that F_2 already contains a contribution from the polarization. This effect is predicted to be weaker for K^+ than for H^+, because of the larger distance between the charge and the induced dipole in the former case. Attention must be drawn to the fact that F_2 is not as robust as F_1 (F_2 is more sensitive to change in the solvent set than F_1), lessening the significance of additional minor terms in eq 6. It is noteworthy that the abstract factors F_1 and F_2 are best interpreted from empirical parameters representative of acid–base *interactions* rather than from properties of an isolated molecule. The third factor is of marginal importance and certainly

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(36) A few values have been assumed by us (see footnote *m*, Table I). Some PCA run on matrices including these data yielded results not significantly different from those obtained on the 13 × 10 subset.

(37) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695–808.

(38) Sunner, J.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 6135–6139 and reference cited therein.

(39) Miller, K. J.; Savchik, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7206–7213.

(40) Brown, H. C. *J. Chem. Soc.* **1956**, 1248–1268.

(41) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377–383.

(42) The large electrostatic character of β is apparent from the fact that a coordinate covalency parameter ξ should be used in complement to describe a wide variety of basicity-dependent phenomena.[16]

(43) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223–234 and references cited therein. We used dipole moments, ionization energies, EHT-HOMO energies,[13] molar refractivities, and their reasonable combinations.

(44) The explanation of F_1 using PA and α: $F_1 = a\text{PA} + b\alpha + c$ has less statistical significance, due to the high degree of correlation between PA and α.

(45) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1976**, *98*, 4400–4404. Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294–300.

(46) Arnett, E. M. In *Proton-Transfer Reactions*; Caldin, E. F., Gold, V. Eds.; Chapman and Hall: New York, 1975; Chapter 3.

(47) Ab initio calculations: (a) Kollman, P.; Rothenberg, S. *J. Am. Chem. Soc.* **1977**, *99*, 1333–1342. (b) Ikuta, S. *Chem. Phys. Lett.* **1985**, *116*, 482–486. Extension of the *E* and *C* approach to gas-phase ion-molecule enthalpies: (c) Kroeger, M. K.; Drago, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 3250–3262.

(48) For this restricted subset, the orthogonality between F_1 and F_2 remains high: r = 0.26.

Table VII. Coordinates of the 22 Solvents along the Three Principal Axes and Properties Related to Their Physical Meaning

solvent	F_1	F_2	F_3[a]	PA[b]	KA[c]	$\alpha_{(ahc)}$[d]	FS[e]
3	-0.89	0.01	*-0.12*	809.0		12.26	
12	-0.57	-0.04	*-0.06*	788.0	100.4	4.42	
25	-0.52	-0.02	*0.04*			11.46	
31	-0.37	-0.16	*-0.01*	811.0		8.79	w
35	-0.44	-0.02	*0.03*	840.0		8.88	
36	-0.37	-0.02	*-0.01*	823.0	108.8	6.33	w
39	-0.34	0.01	*-0.02*	843.0		11.12	w
45	-0.29	-0.11	*-0.03*	838.0	92.0	8.79	m
47	-0.08	0.24	*-0.10*	887.0		11.83	
50	-0.21	-0.04	*0.03*	831.0		8.06	w
52	0.47	-0.10	*-0.22*	955.0		13.16	s
54	0.53	-0.07	*-0.22*			15.01	s
55	0.15	0.20	*0.01*	884.0	146.4	8.03	w
57	0.20	0.11	*0.09*			13.06	m
58	0.11	-0.40	*0.13*	935.0		15.60	
59	0.05	0.12	*0.14*	884.0	129.7	7.86	w
62	0.18	0.15	*0.09*	907.0	129.7	9.70	w
63	0.15	0.16	*0.11*	907.0		10.81	
68	0.48	0.38	*-0.06*			19.64	
72	0.42	-0.08	*0.11*	924.0	87.9	9.47	w
74	0.49	-0.05	*0.13*	942.0		11.32	w
75	0.85	-0.26	*-0.06*	972.0	83.7	13.34	m

[a] Italicized values draw attention to the marginal importance of F_3 compared to F_1 and F_2. [b] Absolute proton affinities from the critical compilation of Lias et al.[37] in kJ·mol^{-1}. [c] Absolute potassium-ion affinities[38] in kJ·mol^{-1}. KA for Et$_3$N (**75**) is assumed to be the same as for Me$_3$N. [d] Average molecular polarizabilities calculated according to the empirical approach of Miller and Savchik[39] in (10^{-1} nm)^3. [e] Front strain[40] evaluated qualitatively (w, weak; m, medium, s, strong) by comparisons within families.

participates in the reproduction of experimental errors. However, its major contribution (see Table III) comes from $-\Delta H^\circ_{BF_3}$ which is one of the more precise and accurate scales but well-known to contain steric effects.[49a-c] Steric hindrance to complex formation seems therefore to contribute to F_3. This is confirmed by the significant increase in the part of variance in the data, explained by F_3, when hindered bases are added to the solvent set (Table VI). Examination of factors in Table VII for pyridine **72** and methyl-substituted pyridines **52**, **54**, and **74** shows that corresponding F_1 and F_2 values are *practically free* from steric strain which is taken into account by F_3. *Differences* in F_3 values for solvents belonging *to a same family*[49d] and qualitatively classified as bases with weak, medium, and strong front strain[40] (see FS in Table VII) confirm that the qualitative chemical interpretation of the third factor is sound. Nevertheless, the very low mathematical significance of F_3, as it stands, precludes its use as a quantitative FS scale though it may be used to describe $-\Delta H^\circ_{BF_3}$, as shown later. It may be possible to assess the F_3 significance by adding more BDPs and molecules sensitive to FS in the basic matrix.

F_1 and F_2 as a Tool for the Analysis of Basicity-Dependent Properties

For most solvents, the front strain is not one of the factors governing their basicity. So, neglecting the third component allows a convenient two-parameter MLR representation of the BDPs.

If the data base from which F_1 and F_2 were obtained is representative of nonprotogenic solvent-basicity effects in general, we expect correlations of the form

$$\mathrm{BDP} = S_1F_1 + S_2F_2 + \mathrm{BDP}_0 \qquad (7)$$

We have examined more than 70 BDPs by using eq 7.

Precise fits are obtained when the following conditions are met:

(1) If only a restricted data is available, care should be exercised that the various classes of solvents are represented. This maintains the necessary orthogonality between F_1 and F_2.

(2) If the reference acid is a well-known candidate to front strain, obviously hindered solvents must be excluded to keep a two-parameter equation.

We have found that S_1 and S_2 in eq 7 (the sensitivities to F_1 and F_2, respectively) vary widely among the various BDPs. Each BDP may be represented by a point on coordinates S_1 and S_2 in the Cartesian plane. In polar coordinates, the corresponding vector has a module $\rho = (S_1^2 + S_2^2)^{1/2}$ and is at angle $\theta = \tan^{-1} S_2/S_1$ with S_1.[50] When the sign of BDP values is chosen to represent an increase in basic strength (chemical feeling) that is in the same sense as F_1, S_1 is always positive. S_2 may be positive or negative. Therefore, θ varies between −90° and +90°. If θ is close to 0°, the BDP presents a character like that of F_1 (electrostatic + charge transfer). An increase of θ corresponds to larger dependence on F_2 and a more electrostatic character. Conversely negative values of θ come from $S_2 < 0$ (anticorrelation with F_2). This is tantamount subtracting a part of the electrostatic component to F_1, resulting in a larger charge-transfer character. Hereafter we present the salient features of our contribution to the interpretation of solvent-basicity effects.

Comparison of Acids by the Use of the Same BDP. Among the various basicity parameters, the enthalpy of complexation is most directly related to the coordinate-bond energy. We sampled eight acids of a priori different characters and submitted their enthalpies of complexation to MLR according to eq 7 (Table VIII). Enthalpies for two acids (BF$_3$, HSO$_3$F) contribute to establish F_1 and F_2. As expected, the square of R (coefficient of determination: fraction of the total variance in the data explained by eq 7) is close to the value of the variance explained by F_1 and F_2 (see Table VI). The fit obtained for other acids is also satisfactory. Comparisons between the different S_1 values

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(49) (a) Azzaro, M.; Derrieu, G.; Elegant, L.; Gal, J.-F. *J. Org. Chem.* **1975**, *40*, 3155–3157. (b) Berthelot, M.; Gal, J.-F.; Laurence, C.; Maria, P.-C. *J. Chim. Phys., Phys. Chim. Biol.* **1984**, *81*, 327–331. (c) Berthelot, M.; Gal, J.-F.; Helbert, M.; Laurence, C.; Maria, P.-C. *J. Chim. Phys., Phys. Chim. Biol.* **1985**, *82*, 427–432. (d) Zero value is the "barycenter" of all the differences in F_3 values for *similar* compounds. The medium FS exhibited by Et$_2$O (**45**) when compared to THF (**50**) is clearly evidenced. F_3 values for pyridines are approximately centered on –005; thus, the –0.06 value for Et$_3$N (**75**) coroborates the existence of the medium FS exibited by this compound when compared to quinuclidine, a similar strong base (not included in the present study) but with relatively small steric requirement resembling those of pyridine. In turn the –0.06 value for CH$_3$CN (**12**) confirms the expected weakness of FS[49e] due to the linearity of the cyano group (in the absence of similar compounds with different steric requirements, F_3 is given a mean value not far from zero). (e) Maria, P.-C.; Gal, J.-F.; Taft, R. W., submitted for publication in *Nouv. J. Chim.* (deals with $-\Delta H^\circ_{BF_3}$ for nitriles compared to their PA).

(50) A similar representation was proposed by Drago; Drago, R. S. *Inorg. Chem.* **1973**, *12*, 2211–2212. ρ has the unit of the BDP and is only useful if one compares the same property in the same unit. If F_3 contributes significantly to a BDP, ρ is underestimated.

(51) Drago, R. S.; Vogel, G. C.; Needham, T. E. *J. Am. Chem. Soc.* **1971**, *93*, 6014–6026.

(52) Purcell, K. F.; Stikeleather, J. A.; Brunk, S. D. *J. Am. Chem. Soc.* **1969**, *91*, 4019–4027.

Table VIII. Dual-Parameter Correlations between Enthalpies[a] and Principal Factors, F_1 and F_2, by Use of Equation 7

acid	S_1[b]	S_2[b]	BDP_0[c]	n[d]	R[e]	s[c,f]	θ[g]
$CHCl_3$[h]	5.8 ± 0.6	10.2 ± 1.5	18.1	6	0.9888	0.7	60
PFP[i]	14.2 ± 1.2	12.8 ± 2.8	26.8	21	0.9471	2.2	42
$SbCl_5$[j]	69.4 ± 4.0	58.6 ± 11.1	100.1	18	0.9808	7.0	40
HFIP[k]	12.5 ± 1.0	7.0 ± 2.7	33.1	10	0.9798	1.4	29
BF_3[l]	59.7 ± 3.4	−4.1 ± 8.4	97.9	20	0.9733	6.4	−4
HSO_3F[m]	103.8 ± 4.9	−42.5 ± 14.2	116.8	21	0.9821	9.5	−22
SO_2[n]	23.8 ± 4.2	−24.1 ± 9.6	44.4	10	0.9216	5.1	−45
I_2[o]	23.5 ± 1.5	−29.5 ± 3.7	21.6	16	0.9813	2.4	−51

[a] $-\Delta H°$ in kJ·mol^{-1}. [b] Uncertainties are standard deviations. [c] In kJ·mol^{-1}. [d] Number of solvents. [e] Correlation coefficient. [f] Standard deviation. [g] $\theta = \tan^{-1}(S_2/S_1)$ in degrees; see text. [h] Measured in cyclohexane, ref 51; solvents, **35**, **36**, **50**, **68**, **72**, **75**; in spite of the small data set the principal classes of solvents are represented, $r(F_1, F_2) = 0.0765$. [i] Mainly from the pure base method; see footnote *g* to Table I. [j] See footnote *d* to Table I, estimated values excluded. [k] Measured in CCl_4, ref 52; solvents, **12**, **35**, **36**, **45**, **54**, **55**, **59**, **68**, **72**, **75**. [l] See footnote *c* to Table I, hindered pyridines **52** and **54** excluded. See text. S_2 is not significant, a contrario, $-\Delta H°_{BF_3}$ is best explained by F_1 and F_3, $-\Delta H°_{BF_3} = (53.2 \pm 1.5)F_1 + (88.5 \pm 6.4)F_3 + 96.1$. $n = 22$, $R = 0.9934$, $s = 3.0$. [m] See footnote *l* to Table I, estimated values excluded. [n] Solution of gaseous SO_2 in bulk solvents, ref 19; solvents, **3**, **12**, **25**, **35**, **47**, **50**, **55**, **58**, **59**, **72**. Pyridine **72**, excluded, $R = 0.9620$, $\theta = -43°$. [o] See footnote *e* to Table I, estimated values excluded.

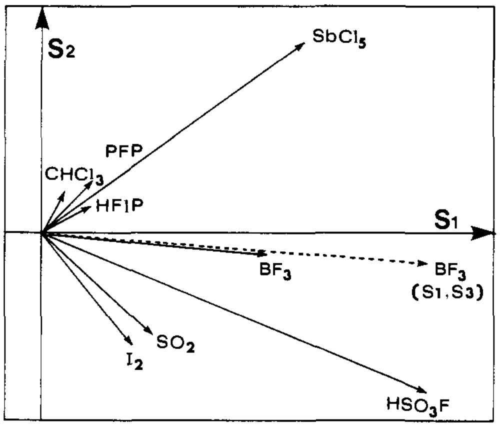

Figure 1. Geometrical representation of complexation enthalpies in the plane of sensitivities (S_1, S_2) to factors F_1 and F_2, respectively (eq 7). The dashed line vector for BF_3, corresponding to a representation in the plane (S_1, S_3) is superimposed on the solid line vector in the plane (S_1, S_2) for comparison purposes.

or S_2 values are legitimate in this particular case because we intentionally treated only enthalpies expressed in the same unit. We observe large changes in sensitivities (absolute values of S) when going from weak to strong acids. S_1 and S_2 may be used to define quantitatively the acid "strength" through the polar coordinate ρ (vide supra). As the electrostatic/charge-transfer (ES/CT) character is defined by θ, a complete picture of the acids' behavior is displayed in Figure 1, where $\Delta H°$ sensitivities toward F_1 and F_2 are represented.

Among the eight acids, we distinguish three classes of strength: (i) weak, with hydrogen-bond donors (HBDs) PFP, HFIP, and $CHCl_3$; (ii) medium, with SO_2 and I_2; and (iii) strong, with Lewis acids with a hard acidic site, e.g., HSO_3F, $SbCl_5$, and BF_3. The moderate strength of BF_3 in the plane (S_1, S_2) (see the solid line vector for BF_3 in Figure 1) is partially misleading. This result has been obtained by excluding hindered pyridines. When these compounds are included in the data set, it is necessary to use F_3 (F_2, insignificant, not taken into account; see the equation in footnote 1, Table VIII). A longer vector, $\rho' = (S_1^2 + S_3^2)^{1/2}$, is obtained (dashed line in Figure 1). So the BF_3 acid strength exhibits a magnitude comparable to that of HSO_3F and $SbCl_5$. The fan-shaped distribution of the vectors corresponds to a large variation of θ which allows an estimate of the ES/CT character of acids as probed by enthalpies of complexation. The observed θ values and the electrostatic/covalent ratios proposed earlier [E_A/C_A,[15,53] $I_2 \simeq SO_2 < BF_3 <$ PFP $\simeq$ HFIP $< CHCl_3$; b/e,[16b] $I_2 <$ proton transfer (condensed phases) $< BF_3 <$ HBD] show the same trend.

Table IX. Variations in θ Values Associated with Changes of BDP Probes in the Case of Hydrogen Bonding

HBD	BDP	θ[a]	R[b]
PFP[c]	$-\Delta G°$	69	0.9916
	$-\Delta H°$	18	0.9603
	$\Delta\nu_{OH}$	−35	0.9697
	$-\Delta S°$	−69	0.9064
TFE[d]	$-\Delta G°$	57	0.9840
	$-\Delta H°$	−12	0.9789
	$\Delta\nu_{OH}$	−19	0.9752
	$-\Delta S°$	−59	0.9523
CYHEX[e]	$-\Delta G°$	72	0.9465
	$-\Delta H°$	7	0.9378
	$\Delta\nu_{OH}$	−36	0.9947
	$-\Delta S°$	−44	0.9172

[a] $\theta = \tan^{-1}(S_2/S_1)$ in degrees; see text. [b] Correlation coefficient in eq 7. [c] *p*-Fluorophenol; all data from Tables VII and VIII in ref 29b, obtained at 298 K in CCl_4, except for a few values for $-\Delta H°$ obtained from the pure base method. Solvents: **12**, **35**, **36**, **39**, **45**, **47**, **50**, **52**, **54**, **55**, **57**, **59**, **62**, **63**, **68**, **72**, **74**, **75**. [d] 2,2,2-Trifluoroethanol; all data from ref 54, obtained at 297 K, in CCl_4, (**12**, **35**, **36**, **45**, **55**, **59**, **62**, **68**) or in hexane (**54**, **72**, **75**). [e] Cyclohexanol; all data from ref 55, obtained at 298 K, in CCl_4 (**12**, **31**, **36**, **50**, **55**, **59**, **72**, except **75** in C_2Cl_4).

ΔG, ΔH, ΔS, and $\Delta\nu_{OH}$ Responses to the Electrostatic/Charge-Transfer Character of Hydrogen Bonding. Hydrogen bonding is an especially useful example of acid–base interaction owing to its fundamental role in natural and synthetic systems. For this reason a vast body of data is available, varying both in reactants and in physicochemical properties. Among the data successfully explained by eq 7, we have chosen three HBDs (parafluorophenol (PFP), 2,2,2-trifluoroethanol (TFE), and cyclohexanol (CYHEX)) for which comprehensive sets of properties of homogeneous origin are available. As we focus on different thermodynamic and spectroscopic properties responses to the ES/CT balance, only the angle θ will be compared (Table IX). We observe that θ, i.e., the ES/CT character, increases in the following order: $-\Delta S° < \Delta\nu_{OH} < -\Delta H° < -\Delta G°$.[56] The entropy of hydrogen-bond formation, as a typical case of intermediate strength interaction, can be viewed as the sum of two terms[22,57]

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(53) For numerical values of E_A and C_A see: (a) Drago, R. S. *Struct. Bonding (Berlin)* **1973**, *15*, 73–139. (b) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251–277, Drago, R. S. *Pure Appl. Chem.* **1980**, *52*, 2261–2274. E_A and C_A for HSO_3F are not available; E_A and C_A given in (a) for $SbCl_5$ calculated from only four enthalpies are excluded in the most recent reviews (b).

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(55) Rossarie, J.; Gallas, J.-P.; Binet, C.; Romanet, R. *J. Chim. Phys., Phys. Chim. Biol.* **1978**, *75*, 63–73.

(56) This trend was confirmed by using more limited and less homogeneous data on the following HBDs; data sources given between parentheses. H_2O ($\Delta G°$, $\Delta H°$, $\Delta\nu_{OH}$, from McTigue, P.; Renowden, P. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1784–1789). C_6H_5OH ($\Delta G°$, Gramstad and coworkers in "Studies of Hydrogen Bonding" parts I to VIII, see: Gramstad, T. *Spectrochim. Acta* **1963**, *15*, 829–834 and preceding papers in the series. Data for nitriles including **12** in part XXIX of the series: Gramstad, T.; Tjessem, K. *J. Mol. Struct.* **1977**, *41*, 231–242. $\Delta H°$, ref 51; $\Delta\nu_{OH}$, footnote *j*, Table I). HFIP ($\Delta H°$, footnote *k*, Table VII; $\Delta\nu_{OH}$, ref 52). $CHCl_3$ ($\Delta G°$, ref 19; $\Delta H°$, footnote *h*, Table VIII).

(57) Person, W. B. *J. Am. Chem. Soc.* **1962**, *84*, 536–540.

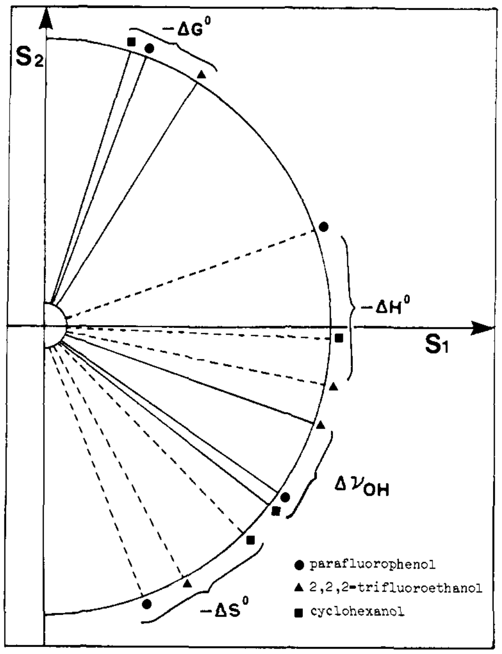

Figure 2. Fan-shaped display of the electrostatic/charge-transfer character of hydrogen-bond basicity-dependent properties. The electrostatic contribution to a BDP increases with θ.

(1) *a large negative* term $\Delta S_{\mathrm{tr.+rot.}}$ due to the loss of translational and rotational degrees of freedom by the system which is *almost constant* depending mainly on the temperature; (2) *a smaller positive* term $\Delta S_{\mathrm{vib.+int.rot.}}$ which was shown to arise essentially from vibrational and internal-rotational degress of freedom due to the formation of the donor–acceptor bond. This contribution is essentially *variable* for intermediate strength complexes due to the low variable frequencies involved and decreases when the donor–acceptor bond is stiffened.

The observed variations in $\Delta S°$ for hydrogen bonding (more generally for all the complexes involved in this study) are therefore attributable to $\Delta S_{\mathrm{vib.+int.rot.}}$.

The fan-shaped display of BDPs on Figure 2 shows that $\Delta S°$ are positioned at the most negative θ values, and therefore entropy appears as the property that is the most sensitive to the charge-transfer character of the hydrogen bond.

The preceding remarks suggest that the high sensitivity of $\Delta S°$ to CT is related to variations of stiffness in donor–acceptor bonds involved in complexes of intermediate strength. On the other hand, the ES effect which is a longer range interaction[58,59] is a minor contribution to $\Delta S°$. So $\Delta S°$, depending on a short-range interaction (charge transfer), appears as a probe localized on the donor–acceptor bond.

Turning anticlockwise on the fan-shaped display of Figure 2, we encounter the IR O–H stretching frequency shifts, $\Delta\nu_{\mathrm{OH}}$ (free minus hydrogen bonded). The O–H bond, contiguous to the hydrogen bond, has a stretching frequency that is a little more sensitive to long-range interaction (increased dependence on electrostatic effect), as compared with $\Delta S°$.

Recent accurate frequency shifts for methanol[49b,c,60] confirm the range of observed θ for $\Delta\nu_{\mathrm{OH}}$, as seen in Table X, and serve to point out subtle structural and medium effects. In some instances, the IR ν_{OH} absorption of C=C- - -HO complexes is made up of two components of high and low frequencies attributable to linear and angular geometry, respectively. These geometries were established in the case of methanol where only one type of adduct is generally observed.[49c] We can observe the structural effects on the F_1, F_2 treatment results by including in the data set carbonyls of either angular or linear adduct structure. When carbonyl compounds giving angular complexes are taken into account, virtually no change is observed (equally good fits, same θ values) as seen in Table X. On the contrary, carbonyl compounds giving linear complexes worsen the fit and shift the θ angle. The linear complexes have a hydrogen bond not directed toward the basic-solvent lone pair, which explains their deviation (too small $\Delta\nu_{\mathrm{OH}}$) from the correlation obtained for the general case (hydrogen bond in the direction of the lone pair).[61] We draw attention to the bias that may be introduced in correlations using $\Delta\nu_{\mathrm{OH}}$ where carbonyl compounds giving linear adducts are concerned.

Table X Structural and Medium Effects on Methanol $\Delta\nu_{\mathrm{OH}}{}^{a}$ Sensitivity toward ES/CT

effect		θ^{b}	n^{c}	R^{d}
structural^{e}		−20	14	0.9923
		−20	16	0.9930
		−30	20	0.9750
medium^{f}	CCl_4	−20	13	0.9927
	bulk	−7	13	0.9909

[a] Data sources: ref 49b, 49c, 60 and personal communication from Prof. Berthelot. $\Delta\nu_{\mathrm{OH}}$ (**50**, in CCl_4) = 158 cm^{-1}. [b] $\theta = \tan^{-1}(S_2/S_1)$ in degrees. [c] Number of solvents. [d] Correlation coefficient of eq 7. [e] n = 14: all solvents except carbonyls. n = 16: carbonyls forming angular hydrogen bond[49c] (**36** and **39**) added. n = 20: carbonyls forming linear hydrogen bond[49c] (**25**, **35**, **57**, **59**, **62**, **63**) added to the 14 non-carbonyls. [f] Data set: **3**, **12**, **31**, **36**, **45**, **47**, **54**, **55**, **58**, **68**, **72**, **74**, **75** (no carbonyl with linear hydrogen bond).

Table XI, Analysis of (β,ξ) and (E_B,C_B) Scales

BDP	θ^{a}	n^{b}	R^{c}
$pK_{HB}{}^{d}$	70	16	0.9983
$\Delta^{19}F_{PFP}{}^{e}$	66	15^{f}	0.9789
$\log K_{PhOH}{}^{g}$	67	14^{h}	0.9947
$-\Delta\Delta\bar{\nu}(NH)^{i}$	66	16	0.9577
$-\Delta\Delta\bar{\nu}(OH)^{j}$	2	16	0.9910
β^{k}	67	16	0.9860
ξ^{k}	−72	15^{l}	0.9869
$E_B{}^{m}$	77	14^{n}	0.9702
$C_B{}^{m}$	−61	14^{n}	0.9762

[a] $\tan^{-1}(S_2/S_1)$ in degrees, see text. [b] Number of solvents; if n = 16, solvents **12**, **31**, **35**, **36**, **39**, **45**, **47**, **50**, **55**, **57**, **59**, **62**, **68**, **72**, **74**, **75**. [c] Correlation coefficient of eq 7. [d] See Table I. [e] Limiting ^{19}F NMR shifts of PFP complexes.[67] [f] **36** not available. [g] From association constants with phenol in CCl_4 at 293 K measured by Gramstad and coworkers, see ref 56: C_6H_5OH, ΔG. [h] **31**, **57**, **62** not available, **63** added; including hindered pyridines **52**, **54**, (log K available), n = 16; R = 0.9929, θ = 67°. [i] Solvatochromic hydrogen-bonding shift (*p*-nitroaniline, *p*-nitro-*N*,*N*-dimethylaniline), $-\Delta\Delta\bar{\nu}(3-5)$ in ref 69. [j] Solvatochromic hydrogen-bonding shift (*p*-nitrophenol, *p*-nitroanisole), $-\Delta\Delta\bar{\nu}$-(1–2) in ref 69. [k] Reference 14. [l] **12** not available. [m] Definitions and data in references cited in ref 53. [n] **39** not available; **31** excluded, strongly deviating in the E_B scale.

A medium effect can also be considered here by comparing results obtained from methanol, $\Delta\nu_{\mathrm{OH}}$, measured either in CCl_4 or in bulk basic solvents.[60] For the above reasons, no carbonyl, giving linear adduct, was included. In bulk solvents, i.e., with a different medium for each measurement, the sensitivity to ES effect is greater than in a constant environment: CCl_4. This may be considered together with the observation of Berthelot et al.[60] about the enhanced solvent dipolarity effect associated with the use of bulk solvent. The factors, in particular F_2, found their origin in a specific (chemical) interaction, whereas the electrostatic solvation is usually considered as a nonspecific (physical) interaction. In the case of the bulk-solvent-basicity effect, the two

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(61) For these reasons $\Delta\nu_{\mathrm{OH}}$ for MeOH was not included in the basic data matrix. For phenol (or PFP) the high and low frequency bands of carbonyl adducts are both present and distinguishable,[62,63] and compiled $\Delta\nu_{\mathrm{OH}}$[12,29b] values used in Table I are very close to those of the angular adduct.

(62) Fritzsche, H. *Spectrochim. Acta, Part A* **1965**, *21A*, 799–813.

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electrostatic contributions (chemical and physical) seem to be taken into account by F_2.

Next to $\Delta\nu_{OH}$ is the BDP $\Delta H°$ situated closest to the F_1 axis. We ascribe the increased ES character to a reduced sensitivity toward a localized interaction (that is the donor–acceptor bond stiffness and the associated $\Delta S°$) and conversely to a larger dependence on long-range electrostatic forces. In other words, $\Delta H°$ is a more global measure of the acid–base interactions (local and long range) than $\Delta S°$. The ES/CT blend may be noticeably affected by the method of determination. The medium effect follows the trend already noted for $\Delta\nu_{OH}$ of methanol, that is to say, the increase in θ when going from $\Delta H°_{PFP}$ obtained mainly in CCl_4 ($\theta = 18°$, Table IX), to $\Delta H°_{PFP}$ obtained mainly by the pure-base method ($\theta = 42°$, Table VIII).

Care should be taken to avoid bias in enthalpy values when trying to evaluate the ES/CT character. For example, $\Delta H°_{PhOH}$ values (in CCl_4) given by Drago et al.[51] were in part calculated from $\Delta\nu_{OH}$. Using these data, we calculate $\theta = -23°$. This value is far from those of another closely related phenol (PFP: $\theta = +18°$, Table X) but very close to $\theta = -22°$ calculated for $\Delta\nu_{OH}$ of phenol (data in Table I; estimated value for **63**, excluded).

The Gibbs free energies of hydrogen bonding are situated in the upper sector of our fan-shaped diagram (Figure 2). As $\Delta G° = \Delta H° - T\Delta S°$, the dominant CT contribution to $\Delta S°$ is substracted from the ES + CT contribution to $\Delta H°$, giving a dominant ES behavior to $\Delta G°$. In this regard it is interesting to note that θ, as $\Delta G°$ itself, should be temperature dependent. Therefore, Gibbs free energies of the same acid–base reaction measured at different temperatures are not necessarily correlated. $\Delta G°$ was also found to be more sensitive to ES than $\Delta H°$ for acids other than HBDs. For example, we have already seen that $\Delta H°_{I_2}$ (strong CT character) lies at $\theta = -51°$ (Table VIII), a value to be compared with $\theta = -21°$ obtained for $\Delta G°_{I_2}$.[64] The aqueous protonation, of primary interest, exhibits an even larger CT character than iodine complexation. Again we obtain the same order of sensitivity to the ES/CT ratio for the thermodynamic properties: $\Delta H°_{(aqH^+)}$ gives $\theta = -79°$ and $\Delta G°_{(aqH^+)}$, $\theta = -52°$.[65]

Therefore, the order of the ES/CT character measured by θ, $\Delta S° < \Delta H° < \Delta G°$, seems to be of general validity. The case where the difference betweeen $\Delta H°$ and $\Delta G°$ vanishes may be considered as a limit. This situation, corresponding to a nearly constant $\Delta S°$, can be anticipated for extremely weak and extremely strong interactions,[57] such as chloroform hydrogen bonding and gas-phase protonation, respectively.

Analysis of the β–ξ Scales and Comparison with E_B–C_B. It is interesting to return to the discussion of hydrogen-bonding Gibbs free energies, with a particular emphasis on the acid, *p*-fluorophenol (pK_{HB} in Table I, property bringing the largest contribution to F_2, Table VI) because of its implication in the definition of the Kamlet–Taft β parameter[2b] of widespread use.[16a,20a] This scale was obtained by averaging various β_i values corresponding to different BDPs obtained from equilibria and spectroscopic measurements.

In Table XI we compare the five BDPs which were used to define the first averaged β using a homogeneous set of representative solvents. The limiting fluorine NMR shift $\Delta^{19}F$, i.e., the shift of the completely formed complex relative to uncomplexed *p*-FC_6H_4OH, displays $\theta = 66°$ very close to $\theta = 70°$ obtained for pK_{HB}. The same is true for log K_{PhOH}, $\theta = 67°$, and for the solvatochromic hydrogen-bonding shift of *p*-nitroaniline compared to its non-HBD "equivalent" *p*-nitro-*N*,*N* dimethylaniline, $\theta = 66°$. The corresponding values $-\Delta\Delta\bar{\nu}(NH)$ come from recent measurements[68] determined independently from the original values[41] (the original set gives the same θ with 11 solvents). All the preceding θ values compare favorably with $\theta = 67°$ for the averaged β. On the other hand $-\Delta\Delta\bar{\nu}(OH)$ values (*p*-nitrophenol, compared to *p*-nitroanisole) also determined by Laurence et al.[68] do not agree with the corresponding β_2 values from Kamlet and Taft.[41] We obtain $\theta = 2°$ for $-\Delta\Delta\bar{\nu}(OH)$ (Table XI) which departs from the averaged β, though the corresponding Kamlet–Taft β_2 gives $\theta = 66°$ ($n = 11$, $R = 0.9868$). This difference may come from the choice of solvents for fixing the reference line in the solvatochromic comparison method.[41,69] Laurence et al. observed a good family-independent linear correlation between $-\Delta\Delta\bar{\nu}(OH)$ and $\Delta H°_{PFP}$ for 37 solvents.[68,70] So a "$\Delta H°$ behavior" of $-\Delta\Delta\bar{\nu}(OH)$ was proposed. On the other hand, the linear correlations observed between $-\Delta\Delta\bar{\nu}(NH)$ and pK_{HB} or $\Delta^{19}F_{PFP}$, also family-independent, were qualified as fortuitous, but the temperature dependence observed for $-\Delta\Delta\bar{\nu}(NH)$ gives support to a "$\Delta G°$ behavior" for this quantity (this is confirmed by the θ values in Table XI).

Since $-\Delta\Delta\bar{\nu}(OH)$ has little weight in the averaged β, it does not affect significantly the information gained by this scale. We advocate that β presents the ES/CT character of hydrogen-bonding $\Delta G°$ for OH HBDs. In fact, there is also some indication that $\Delta G°$ for NH or CH HBDs (5-fluoroindole, $(n\text{-Bu})_3NH^+$, $CHCl_3$) exhibit the same behavior,[71] but further studies on these systems are needed. The θ values observed for equilibria involving hydroxylic HBDs, 2,2,2-trifluoroethanol and cyclohexanol (Table IX) and *p*-fluorophenol and phenol (Table XI) ($\theta = 67 \pm 10°$), support our view that β ($\theta = 66°$), though coming mainly from NH indicators, is a good descriptor of hydrogen-bonding Gibbs free energies. β appears as a mainly electrostatic parameter, and a comparison with the E_B term of Drago shows a striking similarity (Table XI). Kamlet–Taft have introduced a coordinate covalency parameter ξ[14,16b] to be used in combination with β to enlarge its field of application to BDPs exhibiting a large charge-transfer character. A comparison of ξ with the covalent parameter C_B is in order. As shown in Table XI, a similarity between ξ and C_B is evidenced by their θ values.

Summary and Conclusion

The aim of this work was to determine the inherent dimensionality of the condensed-phase basicity of nonprotogenic organic molecules commonly used as solvents. The choice of the 5 most informative scales using the Information theory led us to perform a principal component analysis on 22 solvents, from which 3 factors emerge. A physical significance of empricial nature was given to the two principal factors by their correlations with gas-phase affinities. A blend of electrostatic and electron-delocalization or charge-transfer character was attributed to the first factor F_1, owing to its colinearity with proton affinity once corrected for the enhanced polarizability effect. The second factor, F_2, correlated with potassium-ion affinity, appears essentially electrostatic. The third factor, of marginal importance arises in part from steric hindrance to complexation (front strain). The angle $\theta = \tan^{-1}(S_2/S_1)$ where S_2 and S_1 are the sensitivities of any BDP to F_2 and F_1, respectively, was proposed as an efficient tool for the characterization of basicity-dependent properties according to their susceptibility to electrostatic/charge-transfer effects. A fan-shaped distribution of θ corresponding to various thermodynamic and spectroscopic properties of a given acid is also observed in the plane defined by S_1 and S_2. We have discussed the role played by $\Delta S°$ of complexation and defined it as a localized probe of short-range interaction. As a consequence of the electrostatic + charge-transfer character of $\Delta H°$, $\Delta G°$ appears to be very sensitive to long-range electrostatic interactions. In closing we presented some evidence that the β parameter behaves like $\Delta G°$ for hydrogen

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(64) $-\Delta G°_{I_2}$ (log K_{I_2}) from Table I; same set as for $-\Delta H°_{I_2}$; $R = 0.9787$.

(65) $n = 8$, solvents: **35**, **36**, **45**, **55**, **62**, **72**, **74**, **75**. $-\Delta H°_{(aqH^+)}$, $R = 0.9666$; $\Delta G°_{(aqH^+)}$, $R = 0.9931$; data source, ref 66.

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(70) The θ value of 2° for $-\Delta\Delta\bar{\nu}(OH)$ is to be favorably compared to $\theta = 18°$ for $\Delta H°_{PFP}$ in Table IX for a reduced set of solvents.

(71) θ values of 79°, 81°, and 56° are obtained for the $-\Delta G°$ of hydrogen bonding to 5-fluoroindole,[72] $(n\text{-Bu})_3NH^+$,[19] and $CHCl_3$,[19] respectively.

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bonding toward OH acids, and this is probably true also for NH and CH acids.

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Conformational Analysis of *N*-(1-Phenylethyl)-Δ^4-thiazoline-2-thiones and Analogues. A ^{1}H NMR, Circular Dichroism, X-ray Crystallographic, and Molecular Mechanics Study

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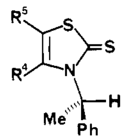
Abstract: The conformations of eleven *N*-(1-phenylethyl)thiazoline-2-thiones and three *N*-(1,2,3,4-tetrahydro-1-naphthyl) analogues with a variety of substituents in positions 4 and 5 have been studied by temperature-dependent ^{1}H NMR and CD spectra, by empirical force-field calculations and in two cases by single-crystal X-ray diffraction. The expected syn–anti equilibrium with respect to the N-substituent is much more biased toward the anti form than in the *N*-isopropyl and *N*-(1-carbomethoxyethyl) analogues. Only the compounds with a 4-phenyl substituent display observable populations of the syn form, and the X-ray diffraction studies show the 4-methyl and 4-phenyl-5-methyl compounds to adopt the anti form in the crystal. Five CD bands in the near UV region are assigned to one $n \rightarrow \pi^*$ and two $\pi \rightarrow \pi^*$ transitions in the thiazolinethione chromophore and to the ^1L_b and ^1L_a transitions in the benzene ring. The temperature dependence of the two thiazoline-thione bands at longest wavelengths for the 4-H compounds is interpreted in terms of an equilibrium between two rotamers within the anti form, by using semiempirical calculations of rotational strengths and experimental temperature-dependent ^{1}H chemical shifts. Corresponding energy minima are found by the molecular mechanics calculations.

A molecular system, composed of a rigid planar framework with an attached sp^3-hybridized atom carrying three different substituents, a chiral rotor, displays a circular dichroism (CD) spectrum, the appearance of which depends on the orientation of the rotor. The signs and magnitudes of the rotational strengths of the electronic transitions in the molecule can in principle be calculated by semiclassical[2] or quantum-chemical[3] methods, if the geometry of the molecule is known. Thus the CD spectrum contains stereochemical information, and this work is a part in a series planned to investigate the possibilities to elucidate the orientation of chiral rotors with respect to planar frameworks by a combined analysis of temperature-dependent CD and NMR spectra.

We have chosen the thiazoline-2-thione system as the planar framework for the following reasons: 1. Its electronic transitions have been studied both experimentally and by CNDO/S[4,5] and PPP[5,6] calculations. 2. The conformations of its *N*-isopropyl and *N*-(1-carboxyethyl) derivatives have been studied by ^{1}H NMR technique.[7,8] 3. It gives rise to a $n \rightarrow \pi^*$ and several $\pi \rightarrow \pi^*$ transitions, and since the rotational strengths of these two kinds of transitions follow different geometric rules,[2] complementary conformational information can be expected.

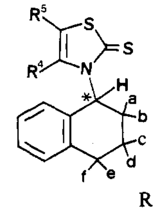
We have chosen a 1-phenylethyl group attached to the nitrogen atom as the chiral rotor, because the transition energies and

Chart I



R^5	R^4: H	Me	Et	*i*-Pr	Ph
H	**1**	**2**		**3**	**4**
Me	**5**	**6**	**7**	**8**	**9**
Ph	**10**	**11**			

Chart II



R^5	R^4: H	Me	Ph
H	**12**	**13**	
Me			**14**

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